meta-C–H Functionalization of Phenylethyl and Benzylic Alcohol Derivatives via Pd/NBE Relay Catalysis

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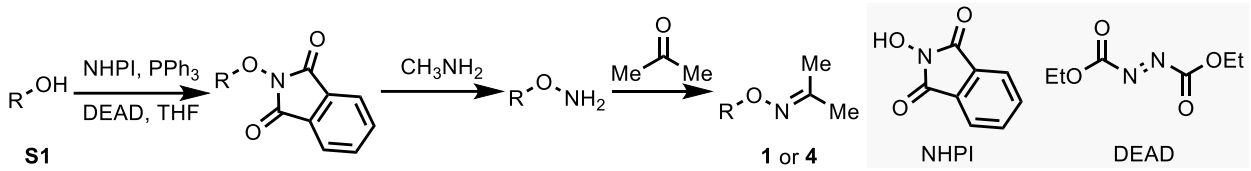
1. General Information

Palladium acetate was purchased from Strem Chemicals. Other reagents were purchased from Alfa Aesar, Sigma-Aldrich, Adamas-beta, J&K Scientific, Aladdin, Bidepharm, Macklin, 9Dingchem, Leyan, Shaoyuan, Meryer, and Energy Chemical of the highest purity grade and used without further purification. The aryl iodide **2w** was synthesized according to the literature[1]. Toluene (tol), Tetrahydrofuran (THF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were dried using the solvent purification system. Other anhydrous solvents were purchased from J&K Scientific. The extent of reaction was monitored by thin-layer chromatography (TLC), performed on 0.25 mm silica gel HSGF254 plates. Visualization was carried out with ultraviolet light (254 nm) or stained with potassium permanganate followed by gentle heating if necessary. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded at room temperature on a Varian 400, Bruker 400 or Agilent 400 (400 MHz for ^{1}H; 375 MHz for ^{19}F; 100 MHz for ^{13}C). The chemical shifts (δ) were quoted in parts per million (ppm) referenced to tetramethylsilane (TMS) (0.0 ppm for ^{1}H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR) and $CFCl_3$ (0.0 ppm for ^{19}F NMR). The following abbreviations were used to explain multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet, br = broad, and coupling constants (*J* Hz). ^{13}C NMR spectra were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF or EI-TOF.

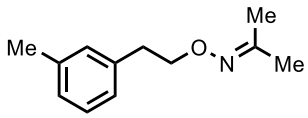
2. Experimental Section

2.1 Preparation of the Substrates



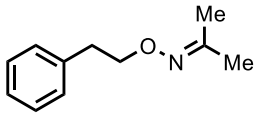
S1d[2], **S1j**[3] and **S1s**[4] were synthesized according to the literature.

General procedure for the preparation of oxime ether from alcohol: To a mixture of the alcohol **S1** (5.0 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (NHPI, 0.9 g, 5.5 mmol, 1.1 equiv.), PPh_3 (1.4 g, 5.5 mmol, 1.1 equiv.) in THF (10 mL) under N_2 atmosphere was added diethyl azodicarboxylate (DEAD, 0.9 mL, 5.5 mmol, 1.1 equiv.) dropwise under an ice-water bath. Then it was allowed to warm to room temperature and stirred overnight. Then methylamine solution (2.5 mL, 25-30 wt. % in water, about 19 mmol, 3.8 equiv.) was added, and the reaction mixture was stirred for 1.0 h. Acetone (2.0 mL, 27.0 mmol, 5 equiv.) was added and the reaction mixture was stirred for another 3.0 h. Then the reaction mixture was diluted with Et_2O and filtered through a pad of celite. The filtrate was concentrated, and the resulting mixture was purified by column chromatography on silica gel with PE/EA to provide the desired product.



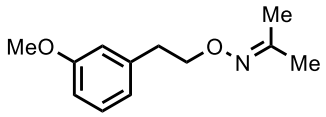
Propan-2-one *O*-(3-methylphenethyl) oxime (1)

Upon purification by the column chromatography on silica gel with PE/EA (60/1 to 40/1) as the eluent, **1** was obtained as a colorless liquid (0.86 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.6 Hz, 1H), 7.06–6.97 (m, 3H), 4.21 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.58, 138.74, 137.68, 129.76, 128.10, 126.75, 125.94, 73.86, 35.68, 21.77, 21.29, 15.54; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1376.



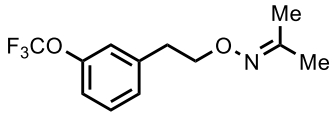
Propan-2-one *O*-phenethyl oxime (4a)[5]

Upon purification by the column chromatography on silica gel with PE/EA (60/1 to 40/1) as the eluent, **4a** was obtained as a colorless liquid (0.88 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.17 (m, 5H), 4.22 (t, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H).



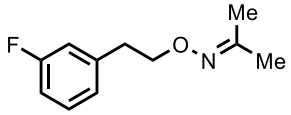
Propan-2-one *O*-(3-methoxyphenethyl) oxime (4c)

4c was synthesized following the general procedure on 6.6 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (25/1 to 15/1) as the eluent, **4c** was obtained as a colorless liquid (0.86 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 6.84–6.72 (m, 3H), 4.22 (t, *J* = 6.8 Hz, 2H), 3.77 (s, 3H), 2.93 (t, *J* = 6.8 Hz, 2H), 1.87 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.49, 154.65, 140.47, 129.15, 121.30, 114.59, 111.43, 73.69, 54.98, 35.80, 21.77, 15.57; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{18}NO_2$ $[M+H]^+$ 208.1332, found 208.1327.



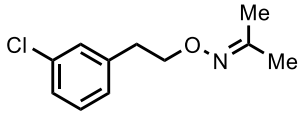
Propan-2-one *O*-(3-(trifluoromethoxy)phenethyl) oxime (4d)

4d was synthesized following the general procedure on 5.2 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (60/1 to 40/1) as the eluent, **4d** was obtained as a pale-yellow liquid (0.94 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.90, 149.20 (q, *J* = 1.0 Hz), 141.52, 129.42, 127.30, 121.53, 120.48 (q, *J* = 255.0 Hz), 118.49, 73.15, 35.43, 21.62, 15.35; ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.19; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{15}NO_2F_3$ $[M+H]^+$ 262.1049, found 262.1042.



Propan-2-one *O*-(3-fluorophenethyl) oxime (4f)

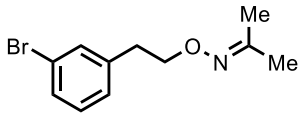
Upon purification by the column chromatography on silica gel with PE/EA (30/1) as the eluent, **4f** was obtained as a colorless liquid (1.0 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (q, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.96–6.84 (m, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 1.87 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.73 (d, *J* = 244.0 Hz), 154.83, 141.59 (d, *J* = 7.0 Hz), 129.55 (d, *J* = 8.0 Hz), 124.53 (d, *J* = 3.0 Hz), 115.78 (d, *J* = 21.0 Hz), 112.86 (d, *J* = 21.0 Hz), 73.26, 35.42 (d, *J* = 2.0 Hz), 21.71, 15.51; ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.43–-114.53 (m); HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{15}NOF$ $[M+H]^+$ 196.1132, found 196.1123.



Propan-2-one *O*-(3-chlorophenethyl) oxime (4g)

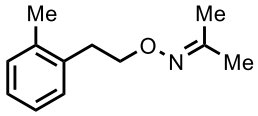
Upon purification by the column chromatography on silica gel with PE/EA (30/1 to 20/1) as the eluent, **4g** was obtained as a colorless liquid (1.0 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.15 (m, 3H), 7.09 (d, *J* = 6.8

Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.03, 141.08, 133.92, 129.45, 129.16, 127.12, 126.23, 73.26, 35.39, 21.82, 15.62; HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{15}NOCl$ $[M+H]^+$ 212.0837, found 212.0830.



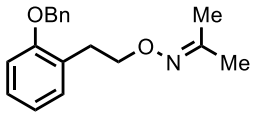
Propan-2-one *O*-(3-bromophenethyl) oxime (4h)

4h was synthesized following the general procedure on 14.7 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (40/1 to 25/1) as the eluent, **4h** was obtained as a colorless liquid (3.8 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.36–7.31 (m, 1H), 7.16–7.12 (m, 2H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.87, 141.37, 132.05, 129.71, 129.09, 127.53, 122.19, 73.20, 35.33, 21.75, 15.55; HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{15}NOBr$ $[M+H]^+$ 256.0332, found 256.0332.



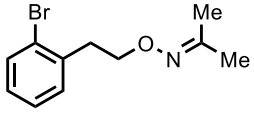
Propan-2-one *O*-(2-methylphenethyl) oxime (4i)

Upon purification by the column chromatography on silica gel with PE/EA (30/1 to 20/1) as the eluent, **4i** was obtained as a colorless liquid (0.29 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.07 (m, 4H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.56, 136.96, 136.33, 130.05, 129.50, 126.21, 125.81, 72.88, 32.97, 21.81, 19.35, 15.58; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1376.



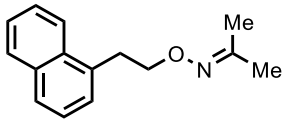
Propan-2-one *O*-(2-(benzyloxy)phenethyl) oxime (4j)

4j was synthesized following the general procedure on 7.6 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (20/1 to 15/1) as the eluent, **4j** was obtained as a colorless liquid (1.8 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21–7.11 (m, 2H), 6.88 (t, *J* = 7.2 Hz, 2H), 5.05 (s, 2H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 1.84 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.61, 154.39, 137.28, 130.77, 128.39, 127.57, 127.46, 127.28, 126.89, 120.48, 111.41, 72.47, 69.57, 30.37, 21.79, 15.53; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1645.



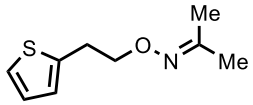
Propan-2-one *O*-(2-bromophenethyl) oxime (4k)

4k was synthesized following the general procedure on 4.1 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (30/1) as the eluent, **4k** was obtained as a colorless liquid (1.1 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.26–7.16 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 6.8 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.64, 138.24, 132.59, 131.05, 127.74, 127.09, 124.59, 71.90, 35.82, 21.73, 15.54; HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{15}NOBr$ $[M+H]^+$ 256.0332, found 256.0332.



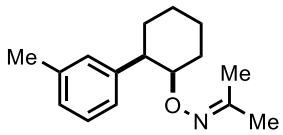
Propan-2-one *O*-(2-(naphthalen-1-yl)ethyl) oxime (4l)

Upon purification by the column chromatography on silica gel with PE/EA (40/1 to 25/1) as the eluent, **4l** was obtained as a colorless liquid (1.1 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.50–7.40 (m, 2H), 7.39–7.33 (m, 2H), 4.36 (t, *J* = 7.2 Hz, 2H), 3.42 (t, *J* = 7.2 Hz, 2H), 1.86 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.68, 134.92, 133.75, 132.15, 128.59, 126.86, 126.78, 125.72, 125.41, 125.36, 123.85, 73.20, 32.81, 21.80, 15.58; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383, found 228.1384.



Propan-2-one *O*-(2-(thiophen-2-yl)ethyl) oxime (4m)

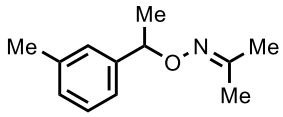
Upon purification by the column chromatography on silica gel with PE/EA (20/1 to 15/1) as the eluent, **4m** was obtained as a colorless liquid (0.84 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.07 (m, 1H), 6.93–6.88 (m, 1H), 6.85–6.80 (m, 1H), 4.23 (t, *J* = 6.8 Hz, 2H), 3.16 (t, *J* = 6.4 Hz, 2H), 1.87 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.89, 141.02, 126.52, 124.97, 123.47, 73.32, 29.80, 21.72, 15.62; HRMS (ESI-TOF) *m/z* Calcd for $C_9H_{14}NOS$ $[M+H]^+$ 184.0791, found 184.0795.



Propan-2-one *O*-(*cis*-2-(*m*-tolyl)cyclohexyl) oxime (4s)

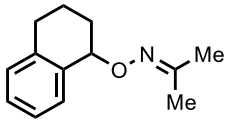
4s was synthesized following the general procedure on 3.6 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (70/1 to 50/1) as the eluent, **4s** was obtained as a pale-yellow liquid (0.24 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.07 (m, 3H), 6.99 (d, *J* = 7.2 Hz, 1H), 4.35 (s, 1H), 2.73 (dt, *J* = 12.8, 2.8 Hz, 1H), 2.32 (s, 3H), 2.21 (d, *J* = 12.4 Hz, 1H), 2.05 (qd, *J* = 12.8, 3.6 Hz, 1H), 1.84 (s, 3H),

1.78 (s, 3H), 1.73–1.64 (m, 1H), 1.57–1.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.50, 144.43, 136.86, 129.00, 127.52, 126.46, 125.08, 79.96, 47.18, 30.45, 26.75, 26.27, 21.66, 21.35, 19.89, 15.46; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{24}NO$ $[M+H]^+$ 246.1852, found 246.1852.



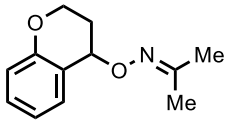
Propan-2-one *O*-(1-(*m*-tolyl)ethyl) oxime (4w)

4w was synthesized following the general procedure on 6.3 mmol scale. Upon purification by the column chromatography on silica gel with PE/DCM (100/1), then PE/EA (20/1) as the eluent, **4w** was obtained as a colorless liquid (0.66 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.14–7.09 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 5.14 (q, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 1.90 (s, 3H), 1.82 (s, 3H), 1.49 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.45, 143.92, 137.66, 128.10, 127.88, 126.78, 123.03, 80.14, 22.40, 21.86, 21.44, 15.76; HRMS (EI-TOF) *m/z* Calcd for $C_{12}H_{17}NO$ $[M]^+$ 191.1305, found 191.1303.



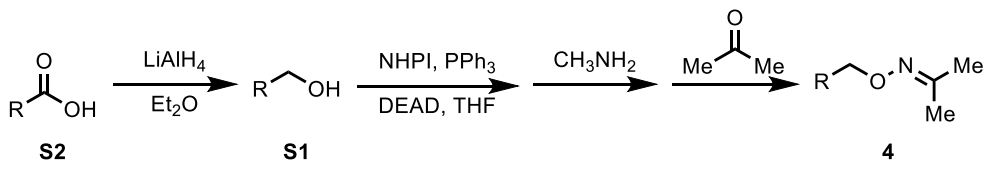
Propan-2-one *O*-(1,2,3,4-tetrahydronaphthalen-1-yl) oxime (4x)[5]

4x was synthesized following the general procedure on 7.6 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (60/1 to 30/1) as the eluent, **4x** was obtained as a colorless liquid (0.58 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 1H), 7.23–7.15 (m, 2H), 7.13–7.09 (m, 1H), 5.14 (t, *J* = 4.4 Hz, 1H), 2.83 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.77–2.67 (m, 1H), 2.17–2.05 (m, 1H), 1.98–1.89 (m, 5H), 1.84 (s, 3H), 1.81–1.71 (m, 1H).



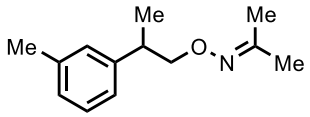
Propan-2-one *O*-chroman-4-yl oxime (4y)[5]

4y was synthesized following the general procedure on 6.1 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (50/1 to 20/1) as the eluent, **4y** was obtained as a colorless liquid (0.61 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 5.09 (t, *J* = 3.6 Hz, 1H), 4.28–4.14 (m, 2H), 2.31–2.22 (m, 1H), 2.16–2.05 (m, 1H), 1.91 (s, 3H), 1.84 (s, 3H).



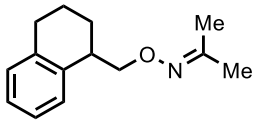
To a solution of the carboxylic acid **S2** (6.0 mmol, 1.0 equiv.) in Et_2O (20 mL) was added $LiAlH_4$ (0.26 g, 6.8 mmol, 1.1 equiv.) portionwise under an ice-water bath. Then the reaction mixture was allowed to warm to room temperature and stirred for 1.0 h. Upon completion, the reaction was quenched by adding H_2O (0.26 mL), 15% NaOH solution (0.26 mL), and H_2O (0.78 mL) sequentially. Then the reaction mixture was filtered through a pad of celite and washed with dichloromethane (DCM). The filtrate was concentrated under vacuum to give the crude product **S1**, which was used directly in the next step without further purification.

To a mixture of **S1** (1.0 equiv.), *N*-hydroxyphthalimide (NHPI, 1.1 equiv.), PPh_3 (1.1 equiv.) in THF (0.5 M) under N_2 atmosphere was added diethyl azodicarboxylate (DEAD, 1.1 equiv.) dropwise under an ice-water bath. Then it was allowed to warm to room temperature and stirred overnight. Then methylamine solution (25-30 wt. % in water, about 3.8 equiv.) was added, and the reaction mixture was stirred for 1.0 h. Acetone (5 equiv.) was added and the reaction mixture was stirred for another 3.0 h. Then the reaction mixture was diluted with Et_2O and filtered through a pad of celite. The filtrate was concentrated, and the resulting mixture was purified by column chromatography on silica gel with PE/EA to provide the desired product.



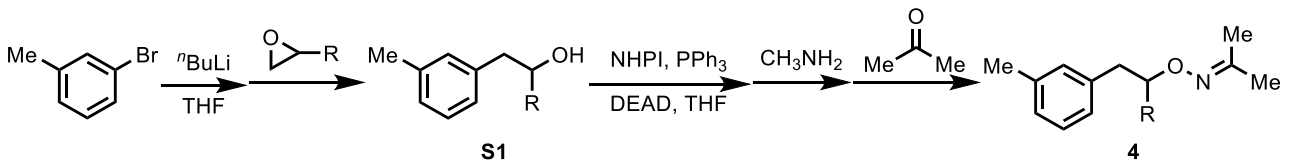
Propan-2-one *O*-(2-(*m*-tolyl)propyl) oxime (4n)

Upon purification by the column chromatography on silica gel with PE/EA (50/1 to 40/1) as the eluent, **4n** was obtained as a colorless liquid (0.61 g, 50% for 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.05–6.99 (m, 3H), 4.12 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.02 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.10 (sext, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.86 (s, 3H), 1.79 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.58, 144.11, 137.64, 128.20, 128.09, 126.92, 124.36, 78.68, 39.14, 21.76, 21.40, 17.90, 15.52; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1537.



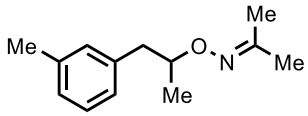
Propan-2-one *O*-((1,2,3,4-tetrahydronaphthalen-1-yl)methyl) oxime (4o)

Upon purification by the column chromatography on silica gel with PE/EA (60/1) as the eluent, **4o** was obtained as a colorless liquid (1.2 g, 93% for 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 7.12–7.03 (m, 3H), 4.23 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.10–4.03 (m, 1H), 3.33–3.16 (m, 1H), 2.81–2.67 (m, 2H), 1.92–1.68 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.35, 137.54, 137.11, 129.13, 128.98, 125.78, 125.36, 77.29, 37.17, 29.57, 25.10, 21.75, 19.37, 15.56; HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{20}NO$ $[M+H]^+$ 218.1539, found 218.1535.



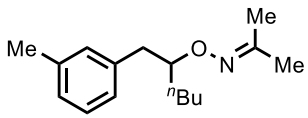
A solution of 3-bromotoluene (1.0 equiv.) in THF (0.67 M) under N_2 atmosphere was cooled to -78 °C, then ^{n}BuLi (2.5 M in hexane, 1.1 equiv.) was added dropwise to the solution. After 1.0 h, the corresponding epoxide (1.1 equiv.) was added dropwise to the reaction mixture at the same temperature, then it was allowed to warm to room temperature. The reaction mixture was stirred overnight and quenched with saturated NH_4Cl solution, diluted with water, extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA to provide **S1**.

To a mixture of **S1** (1.0 equiv.), *N*-hydroxyphthalimide (NHPI, 1.1 equiv.), PPh_3 (1.1 equiv.) in THF (0.5 M) under N_2 atmosphere was added diethyl azodicarboxylate (DEAD, 1.1 equiv.) dropwise under an ice-water bath. Then it was allowed to warm to room temperature and stirred overnight. Then methylamine solution (25-30 wt. % in water, ~3.8 equiv.) was added, and the reaction mixture was stirred for 1.0 h. Acetone (5 equiv.) was added and the reaction mixture was stirred for another 3.0 h. Then the reaction mixture was diluted with Et_2O and filtered through a pad of celite. The filtrate was concentrated, and the resulting mixture was purified by column chromatography on silica gel with PE/EA to provide the desired product.



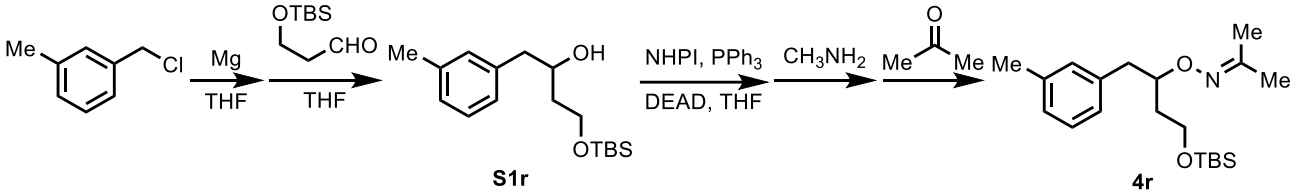
Propan-2-one *O*-(1-(*m*-tolyl)propan-2-yl) oxime (4p)

4p was synthesized following the above procedure on 6.0 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (40/1) as the eluent, **4p** was obtained as a colorless liquid (0.31 g, 25% for 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.2 Hz, 1H), 7.03–6.96 (m, 3H), 4.35 (sext, *J* = 6.0 Hz, 1H), 2.98 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.66 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.31 (s, 3H), 1.86 (s, 3H), 1.82 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.88, 138.64, 137.42, 130.34, 127.90, 126.61, 126.55, 78.86, 42.00, 21.85, 21.30, 19.15, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1533.



Propan-2-one *O*-(1-(*m*-tolyl)hexan-2-yl) oxime (4q)

4q was synthesized following the above procedure on 9.9 mmol scale. Upon purification by the column chromatography on silica gel with PE/EA (80/1 to 60/1) as the eluent, **4q** was obtained as a pale-yellow liquid (0.43 g, 17% for 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.2 Hz, 1H), 7.02–6.96 (m, 3H), 4.21 (quin, *J* = 6.4 Hz, 1H), 2.94 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.74 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.31 (s, 3H), 1.86 (s, 3H), 1.82 (s, 3H), 1.60–1.36 (m, 3H), 1.35–1.23 (m, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.72, 138.90, 137.36, 130.39, 127.84, 126.59, 126.51, 82.82, 40.10, 32.54, 27.68, 22.71, 21.89, 21.33, 15.66, 14.02; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2009, found 248.2008.

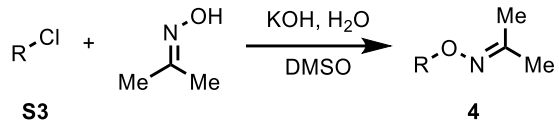


The 100 mL round-bottomed flask was charged with Mg chips (1.5 g, 63 mmol), and was vacuumed and back-filled with N_2 for 3 times. Then, dry THF (4.0 mL) was added, and the reaction mixture was stirred under a water bath. Two drops of 3-methylbenzyl chloride solution (2.6 mL, 20 mmol) in THF (12 mL) was added to initiate the reaction, and then the 3-methylbenzyl chloride solution was added dropwise to afford the Grignard reagent.

A solution of 3-((*tert*-butyldimethylsilyl)oxy)-1-propanal (1.0 g, 5.0 mol) in THF (5.0 mL) was added dropwise to the above prepared Grignard reagent (12.0 mL) under an ice-water bath. Then it was allowed to warm to room temperature and stirred for 4.5 h. Upon completion, the reaction was quenched with saturated NH_4Cl solution, diluted with water, extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA (25/1) to provide a crude product **S1r** (1.0 g, 3.4 mmol) with some minor impurities, which was used for next step without further purification.

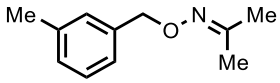
To a mixture of **S1r** prepared above (1.0 g, 3.4 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (NHPI, 0.57 g, 3.5 mmol, 1.0 equiv.), PPh_3 (0.90 g, 3.4 mmol, 1.0 equiv.) in THF (6 mL) under N_2 atmosphere was added diethyl azodicarboxylate (DEAD, 0.54 mL, 3.4 mmol, 1.0 equiv.) dropwise under an ice-water bath. Then it was allowed to warm to room temperature and stirred overnight. Then methylamine solution (2 mL, 25-30 wt. % in water, ~4.5 equiv.) was added, and the reaction mixture was stirred for 1.0 h. Acetone (0.8 mL, 3.2 equiv.) was added and the reaction mixture was stirred for another 3.0 h. Then the reaction mixture was diluted with Et_2O and filtered through a pad of celite. The filtrate was concentrated, and the resulting mixture was purified by column chromatography on silica gel with PE/DCM (100/1 to 20/1), then PE/EA/DCM (60/1/3) to afford **4r** as a colorless liquid (0.80 g, 43% over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.07–7.00 (m, 3H), 4.41 (quin, *J* = 6.4 Hz, 1H), 3.81–3.68 (m, 2H), 3.04 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.84 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.35 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H), 1.80 (q, *J* = 6.8 Hz, 2H), 0.92 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 138.60, 137.38, 130.41, 127.88, 126.64, 126.57, 79.65, 60.01,

40.33, 36.02, 25.92, 21.87, 21.33, 18.27, 15.63, -5.40; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{35}NO_2NaSi$ $[M+Na]^+$ 372.2329, found 372.2325.



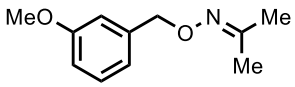
S3 **4**

General procedure for the preparation of oxime ether from benzyl chloride: To a stirred solution of the benzyl chloride **S3** (5.0 mmol, 1.0 equiv.) and acetone oxime (0.4 g, 5.5 mmol, 1.1 equiv.) in DMSO (6.0 mL) was added KOH solution (2.5 mL, 17.8 M in water). After stirring at room temperature for 3.0 h, the reaction was diluted with H_2O, then extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated NaCl solution for 3 times, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA to provide the desired product.



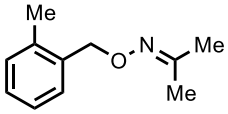
Propan-2-one *O*-(3-methylbenzyl) oxime (4t)

4t was obtained following the general procedure by column chromatography on silica gel with PE/EA (10/1 to 5/1) as a colorless liquid (0.82 g, 92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 1H), 7.18–7.13 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 5.03 (s, 2H), 2.34 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.02, 138.08, 137.78, 128.58, 128.28, 128.13, 124.91, 75.23, 21.81, 21.33, 15.69; HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1228.



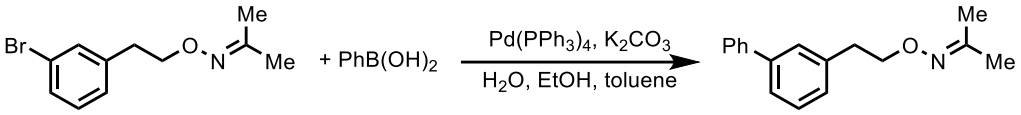
Propan-2-one *O*-(3-methoxybenzyl) oxime (4u)[6]

4u was obtained following the general procedure by column chromatography on silica gel with PE/EA (60/1 to 30/1) as a colorless liquid (0.71 g, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 1H), 6.97–6.89 (m, 2H), 6.83 (dd, *J* = 8.0 Hz, 1H), 5.05 (s, 2H), 3.81 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H).



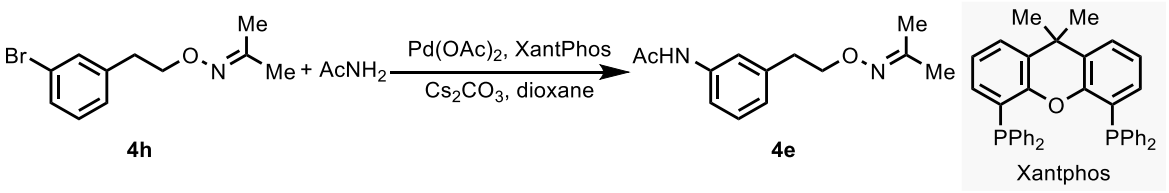
Propan-2-one *O*-(2-methylbenzyl) oxime (4v)[5]

4v was obtained following the general procedure by column chromatography on silica gel with PE/EA (80/1 to 50/1) as a pale-yellow liquid (0.70 g, 79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.2 Hz, 1H), 7.25–7.14 (m, 3H), 5.08 (s, 2H), 2.36 (s, 3H), 1.89 (s, 6H).



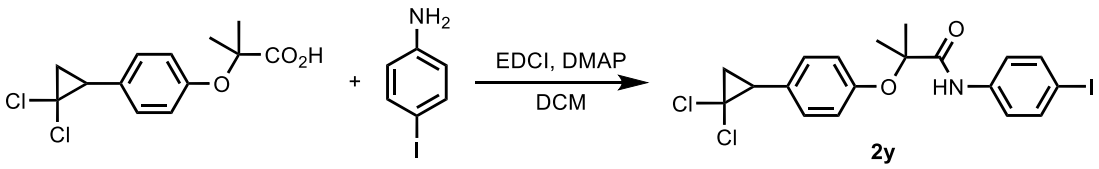
4h **4b**

To a solution of $PhB(OH)_2$ (0.45 g, 3.7 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (87 mg, 0.075 mmol, 2.5 mol %) and **4h** (2.9 mmol, 1.0 equiv.) in toluene (15 mL) and EtOH (15 mL) was added K_2CO_3 solution (1.5 mL, 2.2 M in H_2O). The reaction mixture was heated to 80 °C overnight, then it was cooled to room temperature, filtered through a pad of celite and washed with EA. The solvent was removed under vacuum. The resulting mixture was purified by column chromatography on silica gel with PE/DCM (10/1 to 1/1) then PE/EA (10/1) to provide propan-2-one *O*-(2-([1,1'-biphenyl]-3-yl)ethyl) oxime (**4b**) as a pale-yellow liquid (0.19 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.48–7.38 (m, 4H), 7.37–7.29 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.77, 141.25, 141.22, 139.44, 128.67, 128.65, 127.91, 127.89, 127.13, 127.10, 124.96, 73.81, 35.88, 21.82, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1537.



4h **4e**

$Pd(OAc)_2$ (33 mg, 0.15 mmol, 5 mol %), acetamide (0.25 g, 4.3 mmol, 1.4 equiv.) and Cs_2CO_3 (2.0 g, 6.0 mmol, 2.0 equiv.) was weighted to a sealed tube, then it was moved to a glove box and XantPhos (0.18 g, 0.3 mmol, 10 mol %) was weighted. The tube was removed from the glove box, and dioxane (6.0 mL) and **4h** (0.6 mL, 3.0 mmol, 1.0 equiv.) was added under N_2 atmosphere. The tube was sealed and heated at 120 °C for 27.5 h. Then the reaction mixture was cooled to room temperature, filtered through a pad of celite and washed with ethyl acetate. Silica was added to the filtrate and the solvent was removed under vacuum. The resulting mixture was purified by column chromatography on silica gel with PE/EA (2/1 to 1/2) to provide *N*-(3-(2-((propan-2-ylideneamino)oxy)ethyl)phenyl)acetamide (**4e**) as a yellow solid (0.47 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.41–7.32 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.15 (s, 3H), 1.87 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.42, 155.02, 139.90, 137.91, 128.79, 124.95, 120.37, 117.72, 73.60, 35.69, 24.51, 21.81, 15.66; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{19}N_2O_2$ $[M+H]^+$ 235.1441, found 235.1440.

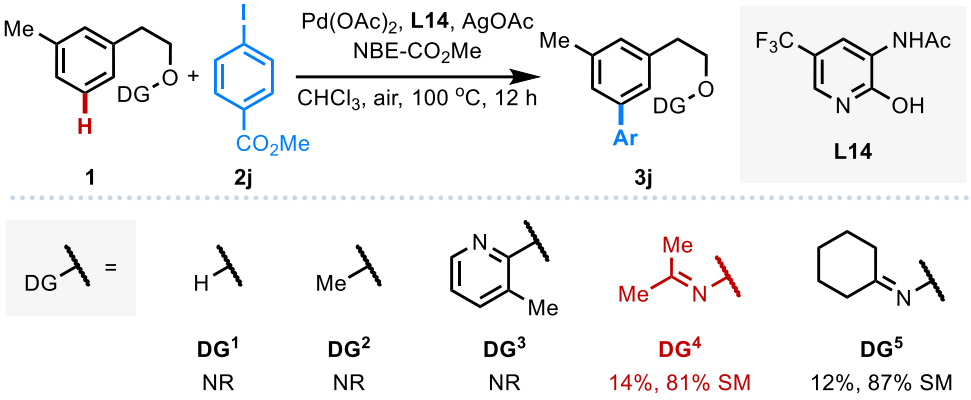


2y

To a stirred solution of ciprofibrate (0.58 g, 2.0 mmol, 1.0 equiv.), 4-iodoaniline (0.45 g, 2.0 mmol, 1.0 equiv.) and DMAP (0.36 g, 3.0 mmol, 1.5 equiv.) in DCM (10 mL) was added EDCI (0.43 g, 2.2 mmol, 1.1 equiv.). After stirring at room temperature overnight, silica was added to the reaction and the solvent was removed under vacuum. The resulting mixture was purified by column chromatography on silica gel with PE/EA (10/1) to provide 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-N-(4-iodophenyl)-2-methylpropanamide (**2y**) as a white solid (0.78 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 2.86 (t, *J* = 9.2 Hz, 1H), 1.97 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.80 (t, *J* = 8.0 Hz, 1H), 1.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.82, 153.12, 137.87, 137.18, 130.25, 129.85, 121.61, 87.61, 82.09, 60.63, 34.74, 25.86, 24.90, 24.86; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{18}NO_2Cl_2INa$ $[M+Na]^+$ 511.9652, found 511.9655.

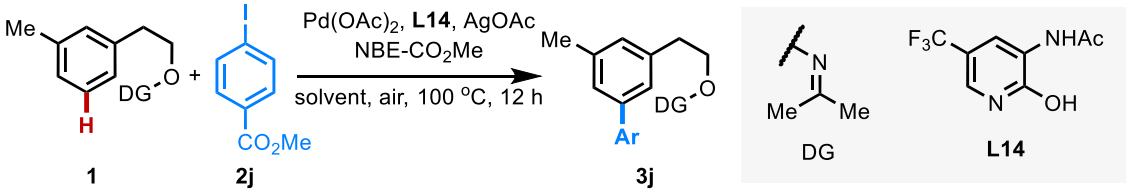
2.2 Optimizations of the Reaction Conditions

Table S1. Screening of the Directing Group[a,b]



[a]**1** (0.1 mmol), **2j** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), **L14** (0.02 mmol), AgOAc (0.15 mmol), NBE-CO_2Me (0.15 mmol), $CHCl_3$ (0.5 mL), air, 100 °C, 12 h. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard.

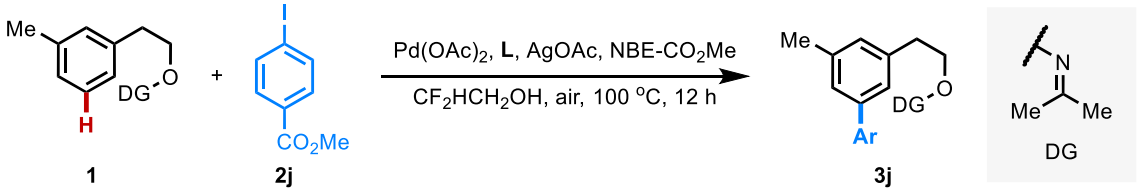
Table S2. Screening of the Solvent[a,b]

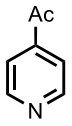
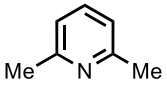
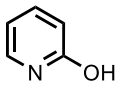
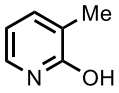
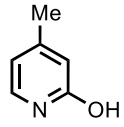
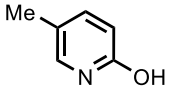
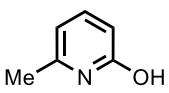
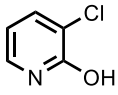
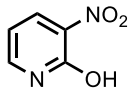
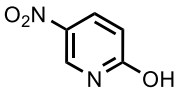
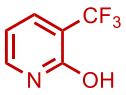
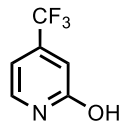
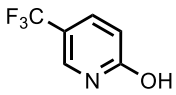
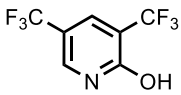
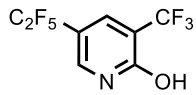
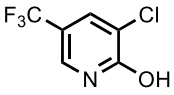
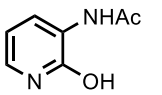
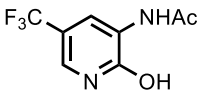


Entry	Solvent	P	SM	Entry	Solvent	P	SM
1	Toluene	44	48	6	CF_2HCH_2OH	85	14
2	Dioxane	34	68	7	TFE	80	3
3	DCE	6	72	8	HFIP	75	11
4	$CHCl_3$	14	81	9	AcOH	38	30
5	^{t}BuOH	36	64	10	EA	37	62

[a]**1** (0.1 mmol), **2j** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), **L14** (0.02 mmol), AgOAc (0.15 mmol), NBE-CO_2Me (0.15 mmol), solvent (0.5 mL), air, 100 °C, 12 h. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard.

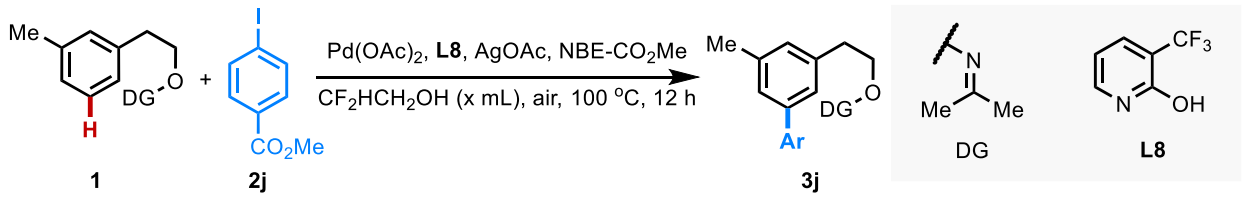
Table S3. Ligands Effects[a,b]



-	Ac-Val-OH			1-AdCOOH		
	L1	**L2**	**LS1**	**L3**	**L4**	**L5**
21%, 79% SM	17%, 80% SM	13%, 82% SM	12%, 83% SM	25%, 70% SM	84%, 16% SM	71%, 18% SM
						
LS2	**LS3**	**LS4**	**L6**	**L7**	**LS5**	**L8**
80%, 19% SM	83%, 14% SM	27%, 68% SM	76%, 22% SM	73%, 21% SM	67%, 26% SM	87%, 13% SM
						
L9	**L10**	**L11**	**L12**	**LS6**	**L13**	**L14**
83%, 17% SM	75%, 15% SM	80%, 20% SM	82%, 17% SM	66%, 22% SM	68%, 30% SM	85%, 14% SM

[a]**1** (0.1 mmol), **2j** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), **L** (0.02 mmol), AgOAc (0.15 mmol), NBE-CO_2Me (0.15 mmol), CF_2HCH_2OH (0.5 mL), air, 100 °C, 12 h. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard.

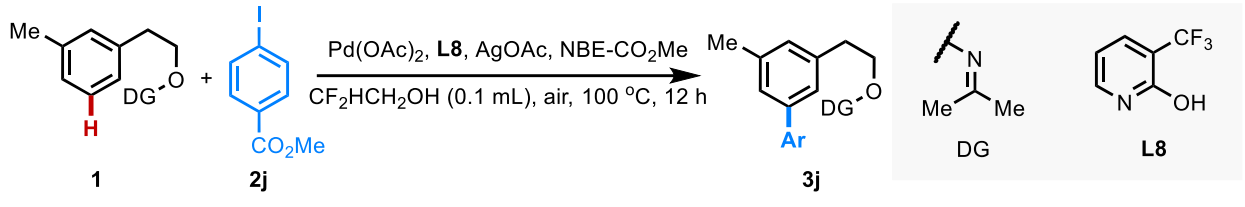
Table S4. Screening of the Concentration[a,b]



Entry	x	P (%)	SM (%)
1	0.5	87	13
2	0.3	90	10
3	0.2	91	9
4	0.1	94(84[c])	6
5	0.05	57	36

[a]**1** (0.1 mmol), **2j** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), **L8** (0.02 mmol), AgOAc (0.15 mmol), NBE-CO_2Me (0.15 mmol), CF_2HCH_2OH (x mL), air, 100 °C, 12 h. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard. [c]Isolated yield on 0.2 mmol scale.

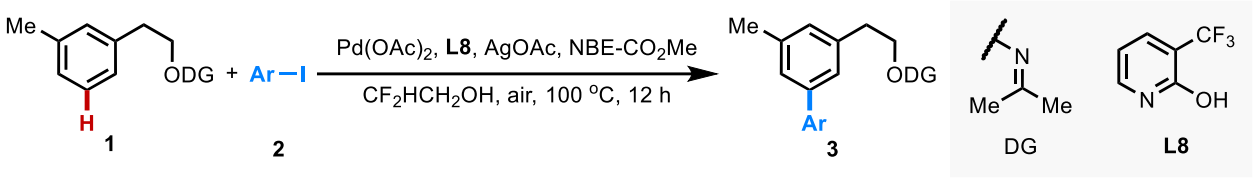
Table S5. Effect of the NBE[a,b]



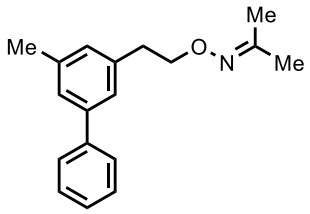
-	NBE	NBE-CO_2Me
0%, 88% SM	5%, 62% SM	94%, 6% SM

[a]**1** (0.1 mmol), **2j** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), **L8** (0.02 mmol), AgOAc (0.15 mmol), NBE (0.15 mmol), CF_2HCH_2OH (x mL), air, 100 ℃, 12 h. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard.

2.3 Evaluation of the Aryl Iodides

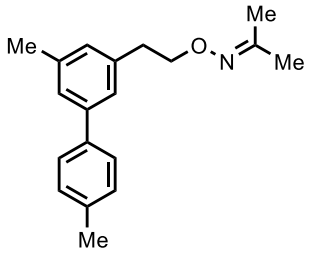


General Procedure for *meta*-C–H Arylation of Aromatic Alcohols: To an 8.0 mL vial were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **L8** (6.5 mg, 0.04 mmol), AgOAc (50.1 mg, 0.3 mmol), **2** (0.3 mmol), CF_2HCH_2OH (0.2 mL), propan-2-one *O*-(3-methylphenethyl) oxime (**1**) (39.5 μL, 0.2 mmol) and NBE-CO_2Me (36 μL, 0.3 mmol). The vial was capped and closed tightly. Then the reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane, filtered through silica and washed with dichloromethane. The resulting solution was concentrated and purified by the preparative thin-layer chromatography (PTLC) or column chromatography on silica gel to afford the desired product.



Propan-2-one *O*-(2-(5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3a)

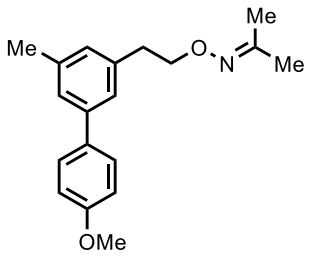
Upon purification by PTLC with PE/EA (20/1) as the eluent, **3a** was obtained as a colorless liquid (32.7 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.26 (s, 1H), 7.25 (s, 1H), 7.04 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.74, 141.38, 141.24, 139.33, 138.22, 128.80, 128.60, 127.12, 127.05, 125.83, 125.06, 73.91, 35.82, 21.84, 21.43, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1694.



Propan-2-one *O*-(2-(4',5-dimethyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3b)

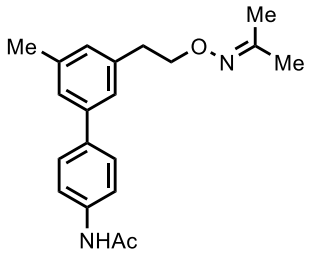
Upon purification by PTLC with PE/EA (20/1) as the eluent, **3b** was obtained as a colorless liquid (39.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.27–7.19 (m, 4H), 7.01 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 6H), 1.88 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.71,

141.14, 139.25, 138.47, 138.15, 136.77, 129.33, 128.53, 126.94, 125.64, 124.86, 73.93, 35.83, 21.83, 21.42, 21.04, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}NO$ $[M+H]^+$ 282.1852, found 282.1853.



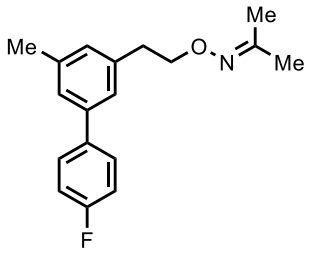
Propan-2-one *O*-(2-(4'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3c)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **3c** was obtained as a colorless liquid (39.9 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.23–7.19 (m, 2H), 6.99 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.25 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.00, 154.71, 140.80, 139.25, 138.16, 133.90, 128.22, 128.09, 125.42, 124.64, 114.05, 73.93, 55.27, 35.83, 21.83, 21.42, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}NO_2$ $[M+H]^+$ 298.1802, found 298.1803.



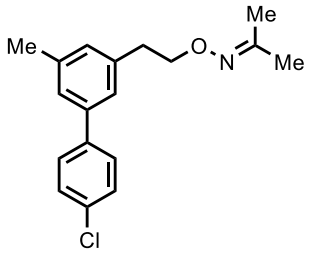
***N*-(3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-yl)acetamide (3d)**

Upon purification by the column chromatography on silica gel with PE/EA (1.5/1) as the eluent, **3d** was obtained as a pale-yellow solid (35.0 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 2H), 7.01 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 2.17 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.47, 154.84, 140.44, 139.32, 138.24, 137.25, 137.10, 128.63, 127.50, 125.48, 124.69, 120.09, 73.86, 35.77, 24.48, 21.80, 21.39, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{25}N_2O_2$ $[M+H]^+$ 325.1911, found 325.1912.



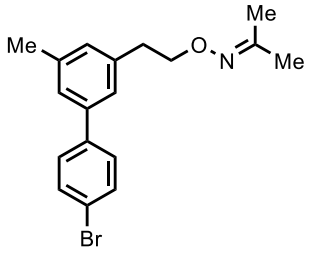
Propan-2-one *O*-(2-(4'-fluoro-5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3e)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3e** was obtained as a colorless liquid (32.5 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2H), 7.20 (s, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 7.03 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.34 (d, *J* = 246.0 Hz), 154.78, 140.24, 139.45, 138.33, 137.48 (d, *J* = 3.0 Hz), 128.81, 128.62 (d, *J* = 8.0 Hz), 125.70, 124.92, 115.44 (d, *J* = 21.0 Hz), 73.88, 35.80, 21.85, 21.41, 15.64; ^{19}F NMR (375 MHz, $CDCl_3$) δ -116.54–-116.64 (m); HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{21}NOF$ $[M+H]^+$ 286.1602, found 286.1602.



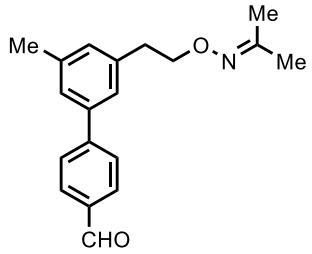
Propan-2-one *O*-(2-(4'-chloro-5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3f)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3f** was obtained as a white solid (43.8 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 1H), 7.20 (s, 1H), 7.04 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.78, 139.95, 139.80, 139.53, 138.39, 133.11, 129.13, 128.74, 128.33, 125.62, 124.85, 73.83, 35.77, 21.84, 21.40, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{21}NOCl$ $[M+H]^+$ 302.1306, found 302.1304.



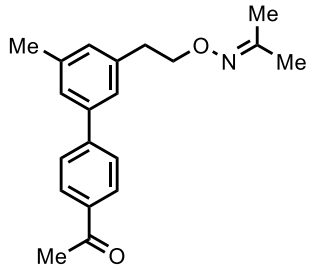
Propan-2-one *O*-(2-(4'-bromo-5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3g)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3g** was obtained as a white solid (44.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 1H), 7.20 (s, 1H), 7.05 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.78, 140.26, 139.95, 139.56, 138.42, 131.69, 129.19, 128.69, 125.58, 124.81, 121.28, 73.83, 35.77, 21.85, 21.41, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{21}NOBr$ $[M+H]^+$ 346.0801, found 346.0793.



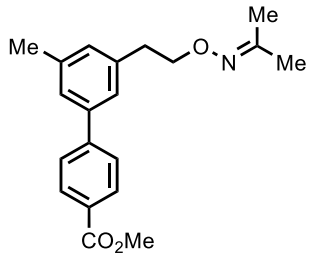
3'-Methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carbaldehyde (3h)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **3h** was obtained as a colorless liquid (27.5 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.29 (s, 1H), 7.10 (s, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.87, 154.84, 147.40, 139.74, 139.69, 138.57, 135.06, 130.14, 130.03, 127.62, 125.98, 125.24, 73.75, 35.74, 21.84, 21.40, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1645, found 296.1639.



1-(3'-Methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3i)

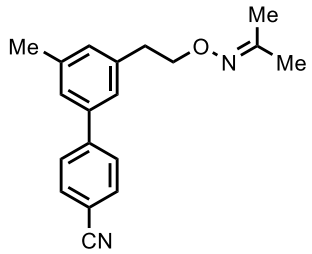
Upon purification by PTLC with PE/EA (9/1) as the eluent, **3i** was obtained as a white solid (44.3 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 1H), 7.28 (s, 1H), 7.09 (s, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.63 (s, 3H), 2.40 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.65, 154.77, 145.94, 139.81, 139.64, 138.47, 135.68, 129.77, 128.76, 127.13, 125.86, 125.12, 73.76, 35.74, 26.57, 21.82, 21.38, 15.61; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_2$ $[M+H]^+$ 310.1802, found 310.1794.



Methyl 3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (3j)

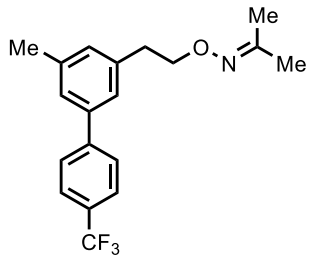
Upon purification by PTLC with PE/EA (9/1) as the eluent, **3j** was obtained as a white solid (54.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.29 (s, 1H), 7.28 (s, 1H), 7.08

(s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.96, 154.76, 145.79, 139.94, 139.60, 138.43, 129.94, 129.67, 128.67, 126.96, 125.87, 125.13, 73.77, 52.00, 35.74, 21.81, 21.37, 15.60; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$ 326.1751, found 326.1743.



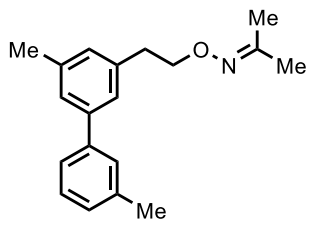
3'-Methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carbonitrile (3k)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **3k** was obtained as a colorless liquid 23.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.26–7.23 (m, 2H), 7.11 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.90, 145.86, 139.87, 139.16, 138.71, 132.44, 130.20, 127.67, 125.84, 125.08, 118.97, 110.65, 73.71, 35.71, 21.85, 21.39, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$ 293.1648, found 293.1640.



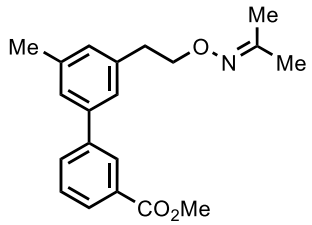
Propan-2-one *O*-(2-(5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethyl) oxime (3l)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **3l** was obtained as a colorless liquid (47.4 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 4H), 7.26 (s, 1H), 7.25 (s, 1H), 7.09 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.84, 144.90, 139.74, 138.56, 129.74, 129.12 (q, *J* = 32.0 Hz), 127.35, 125.91, 125.55 (q, *J* = 4.0 Hz), 125.15, 124.32 (q, *J* = 270.0 Hz), 73.79, 35.76, 21.83, 21.39, 15.62; ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.84; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}NOF_3$ $[M+H]^+$ 336.1570, found 336.1561.



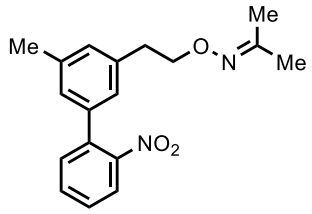
Propan-2-one *O*-(2-(3',5-dimethyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3m)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3m** was obtained as a colorless liquid (36.0 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.89 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.76, 141.33, 141.32, 139.22, 138.14, 138.13, 128.72, 128.51, 127.93, 127.80, 125.82, 125.06, 124.21, 73.93, 35.81, 21.85, 21.50, 21.43, 15.65; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}NO$ $[M+H]^+$ 282.1852, found 282.1862.



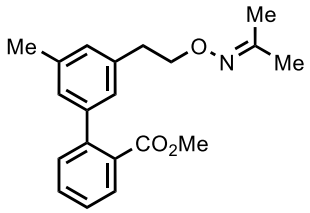
Methyl 3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-3-carboxylate (3n)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **3n** was obtained as a colorless liquid (45.2 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.29 (s, 2H), 7.07 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.04, 154.83, 141.56, 140.02, 139.54, 138.41, 131.47, 130.52, 129.27, 128.68, 128.16, 128.15, 125.76, 125.03, 73.81, 52.11, 35.76, 21.83, 21.39, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$ 326.1751, found 326.1743.



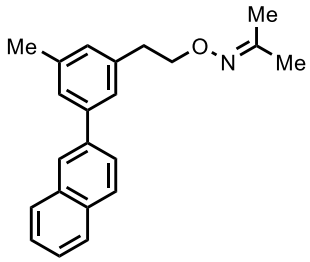
Propan-2-one *O*-(2-(5-methyl-2'-nitro-[1,1'-biphenyl]-3-yl)ethyl) oxime (3o)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **3o** was obtained as a colorless liquid (42.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.58 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48–7.39 (m, 2H), 7.09 (s, 1H), 6.98 (s, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.85, 149.30, 139.38, 138.23, 137.24, 136.47, 132.03, 131.89, 129.77, 127.87, 126.35, 125.64, 123.90, 73.62, 35.59, 21.82, 21.31, 15.60; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1546. **3o** could also be obtained using 1-bromo-2-nitrobenzene instead and following the same procedure (44.1 mg, 71%).



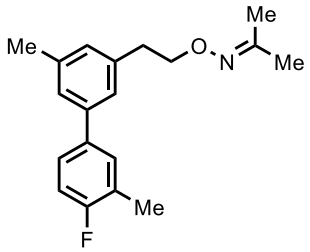
Methyl 3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-2-carboxylate (3p)

Upon purification by PTLC with PE/EA (10/1) then DCM as the eluent, **3p** was obtained as a colorless liquid (36.6 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41–7.32 (m, 2H), 7.03 (s, 1H), 6.98 (s, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 3.63 (s, 3H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.36, 154.75, 142.37, 141.12, 138.55, 137.51, 131.02, 131.00, 130.52, 129.51, 128.81, 126.92, 126.83, 126.11, 73.91, 51.86, 35.67, 21.83, 21.34, 15.61; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$ 326.1751, found 326.1754. **3p** could also be obtained using methyl 2-bromobenzoate instead and following the general *meta*-C–H arylation procedure, purified by PTLC with PE/EA (9/1) as the eluent (46.7 mg, 72%).



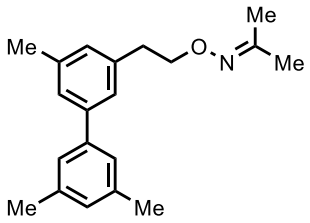
Propan-2-one *O*-(3-methyl-5-(naphthalen-2-yl)phenethyl) oxime (3q)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3q** was obtained as a colorless liquid (42.7 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.90–7.82 (m, 3H), 7.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.51–7.43 (m, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 7.07 (s, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.89 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.76, 141.08, 139.46, 138.70, 138.34, 133.66, 132.56, 128.92, 128.23, 128.11, 127.58, 126.17, 126.07, 125.76, 125.67, 125.65, 125.32, 73.93, 35.86, 21.86, 21.47, 15.66; HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{24}NO$ $[M+H]^+$ 318.1852, found 318.1848.



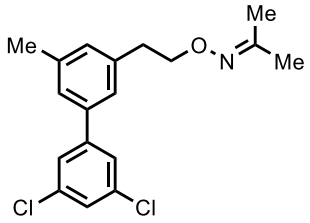
Propan-2-one *O*-(2-(4'-fluoro-3',5-dimethyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3r)

Upon purification by PTLC with PE/EA/DCM (30/1/1) as the eluent, **3r** was obtained as a colorless liquid (37.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 2H), 7.20 (s, 1H), 7.19 (s, 1H), 7.06–7.00 (m, 2H), 4.25 (t, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.90 (d, *J* = 243.0 Hz), 154.79, 140.42, 139.33, 138.25, 137.16 (d, *J* = 4.0 Hz), 130.17 (d, *J* = 6.0 Hz), 128.67, 125.87 (d, *J* = 8.0 Hz), 125.66, 124.89, 124.73, 115.07 (d, *J* = 22.0 Hz), 73.90, 35.79, 21.85, 21.41, 15.64, 14.65 (d, *J* = 4.0 Hz); ^{19}F NMR (375 MHz, $CDCl_3$) δ -120.82–-120.91 (m); HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{23}NOF$ $[M+H]^+$ 300.1758, found 300.1760.



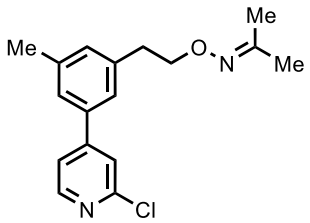
Propan-2-one *O*-(2-(3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3s)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3s** was obtained as a colorless liquid (41.2 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.27 (s, 1H), 7.22 (s, 2H), 7.05 (s, 1H), 7.00 (s, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 6H), 1.92 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.69, 141.42, 141.35, 139.15, 138.05, 128.70, 128.64, 125.81, 125.05, 73.95, 35.82, 21.85, 21.36, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{26}NO$ $[M+H]^+$ 296.2009, found 296.2016.



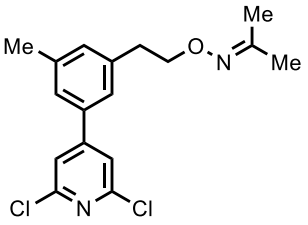
Propan-2-one *O*-(2-(3',5'-dichloro-5-methyl-[1,1'-biphenyl]-3-yl)ethyl) oxime (3t)

Upon purification by PTLC with PE/EA (25/1) as the eluent, **3t** was obtained as a colorless liquid (48.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.30 (s, 1H), 7.20 (s, 1H), 7.19 (s, 1H), 7.08 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.90 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.90, 144.34, 139.80, 138.62, 138.43, 135.07, 129.98, 126.88, 125.62, 125.56, 124.94, 73.71, 35.68, 21.86, 21.38, 15.66; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{20}NOCl_2$ $[M+H]^+$ 336.0917, found 336.0911.



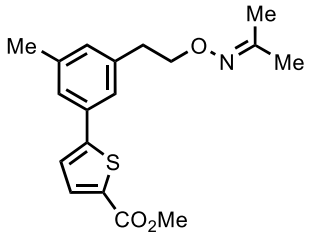
Propan-2-one *O*-(3-(2-chloropyridin-4-yl)-5-methylphenethyl) oxime (3u)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **3u** was obtained as a colorless liquid (24.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.2 Hz, 1H), 7.52 (s, 1H), 7.40 (d, *J* = 4.4 Hz, 1H), 7.29–7.25 (m, 2H), 7.15 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.93, 152.08, 151.80, 149.82, 140.16, 138.92, 136.79, 131.22, 125.58, 124.89, 122.00, 120.45, 73.59, 35.65, 21.83, 21.36, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}N_2OCl$ $[M+H]^+$ 303.1259, found 303.1251.



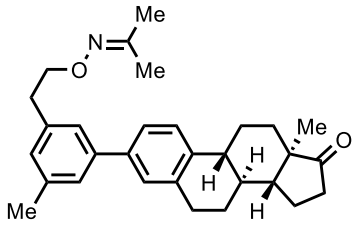
Propan-2-one *O*-(3-(2,6-dichloropyridin-4-yl)-5-methylphenethyl) oxime (3v)

Upon purification by PTLC with PE/EA (20/1) as the eluent, **3v** was obtained as a white solid (58.0 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.25 (s, 1H), 7.24 (s, 1H), 7.17 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.90 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.95, 154.12, 150.81, 140.32, 139.07, 135.56, 131.78, 125.53, 124.87, 120.65, 73.46, 35.55, 21.81, 21.32, 15.61; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{19}N_2OCl_2$ $[M+H]^+$ 337.0869, found 337.0864.



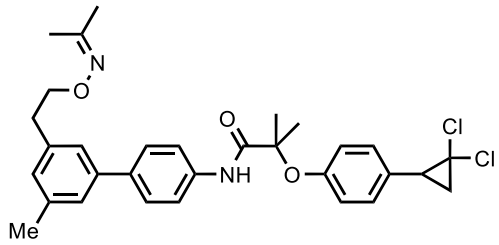
Methyl 5-(3-methyl-5-(2-((propan-2-ylideneamino)oxy)ethyl)phenyl)thiophene-2-carboxylate (3w)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **3w** was obtained as a colorless liquid (33.0 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 4.0 Hz, 1H), 7.30 (s, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.04 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.68, 154.95, 151.63, 139.91, 138.69, 134.29, 133.23, 131.61, 130.42, 124.79, 124.13, 123.35, 73.58, 52.08, 35.60, 21.84, 21.29, 15.66; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{22}NO_3S$ $[M+H]^+$ 332.1315, found 332.1321.



(8*S*,9*R*,13*R*,14*R*)-13-Methyl-3-(3-methyl-5-(2-((propan-2-ylideneamino)oxy)ethyl)phenyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3x)

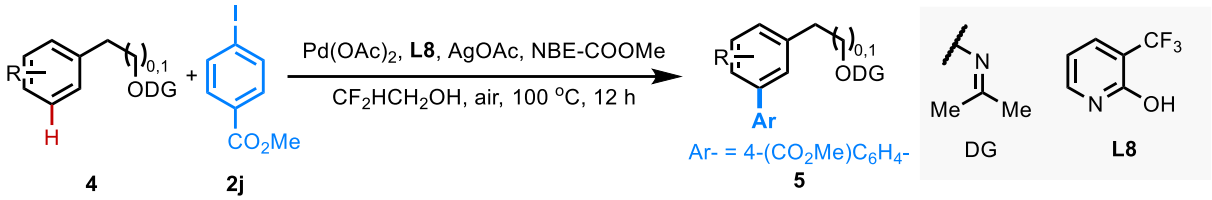
Upon purification by PTLC with PE/EA/DCM (15/1/15) as the eluent, **3x** was obtained as a white solid (52.2 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.31 (s, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.02 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 3.01–2.94 (m, 4H), 2.56–2.42 (m, 2H), 2.38 (s, 3H), 2.35–2.30 (m, 1H), 2.20–1.95 (m, 4H), 1.89 (s, 3H), 1.86 (s, 3H), 1.70–1.44 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.82, 154.75, 140.91, 139.14, 138.82, 138.64, 138.12, 136.65, 128.61, 127.64, 125.65, 125.60, 124.82, 124.47, 73.89, 50.42, 47.93, 44.28, 38.10, 35.79, 35.77, 31.53, 29.47, 26.49, 25.68, 21.85, 21.53, 21.42, 15.65, 13.79; HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{38}NO_2$ $[M+H]^+$ 444.2897, found 444.2891.



2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-methyl-*N*-(3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-yl)propenamide (3y)

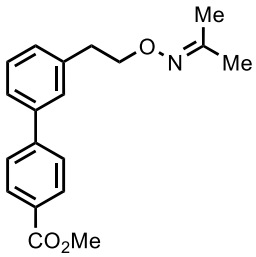
Upon purification by PTLC with PE/EA (9/1) as the eluent, **3y** was obtained as a pale yellow liquid (78.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.26–7.21 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.25 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.85 (dd, *J* = 10.4, 8.4 Hz, 1H), 2.38 (s, 3H), 1.95 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.88 (s, 3H), 1.84 (s, 3H), 1.79 (t, *J* = 8.0 Hz, 1H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.80, 154.78, 153.38, 140.43, 139.43, 138.30, 137.52, 136.61, 130.15, 129.90, 128.75, 124.77, 121.56, 120.00, 82.13, 73.91, 60.71, 35.83, 34.81, 25.89, 25.04, 24.99, 21.88, 21.46, 15.68; HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{35}N_2O_3Cl_2$ $[M+H]^+$ 553.2019, found 553.2014.

2.4 Evaluation of the Aryl Alcohols



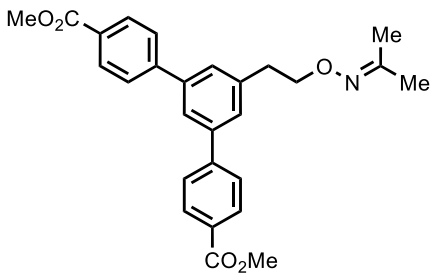
General Procedure for *meta*-C–H Arylation of Aromatic Alcohols: To an 8.0 mL vial were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **L8** (6.5 mg, 0.04 mmol), AgOAc (50.1 mg, 0.3 mmol), methyl 4-iodobenzoate (**2j**) (104.8 mg, 0.3 mmol), CF_2HCH_2OH (0.2 mL), **4** (0.2 mmol) and NBE-CO_2Me (36 μL, 0.3 mmol). The vial was capped and closed tightly. Then the reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane, filtered through silica and washed with dichloromethane. The resulting solution was concentrated and purified by the preparative thin-layer chromatography (PTLC) or column chromatography on silica gel to afford the desired product.

Following the general *meta*-C–H arylation procedure, **5a-mono** was separated by PTLC with PE/EA (9/1), while **5a-di** was separated by PTLC with PE/DCM (1/3).



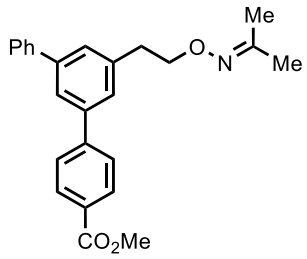
Methyl 3'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5a-mono)

White solid (25.5 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.50–7.44 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.28–7.24 (m, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 3.04 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 154.90, 145.67, 139.96, 139.73, 130.01, 128.84, 128.82, 128.77, 127.99, 126.98, 125.08, 73.70, 52.07, 35.82, 21.84, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_3$ $[M+H]^+$ 312.1594, found 312.1592.



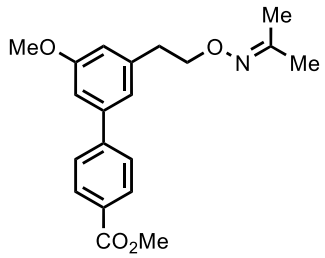
Dimethyl 5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (5a-di)

White solid (25.3 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 4H), 7.72–7.67 (m, 5H), 7.52 (d, *J* = 1.2 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.95 (s, 6H), 3.11 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 154.99, 145.36, 140.79, 140.57, 130.11, 129.10, 127.83, 127.12, 124.21, 73.62, 52.13, 35.88, 21.85, 15.67; HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{28}NO_5$ $[M+H]^+$ 446.1962, found 446.1953.



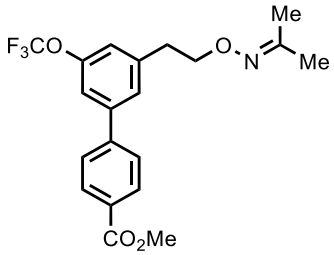
Methyl 5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1':3',1''-terphenyl]-4-carboxylate (5b)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5b** was obtained as a pale-yellow solid (54.0 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.50–7.41 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 1H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.93 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.92, 154.85, 145.62, 141.99, 140.93, 140.52, 140.24, 130.04, 128.93, 128.75, 127.75, 127.43, 127.18, 127.08, 126.94, 124.11, 73.69, 52.05, 35.91, 21.81, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{26}NO_3$ $[M+H]^+$ 388.1907, found 388.1898.



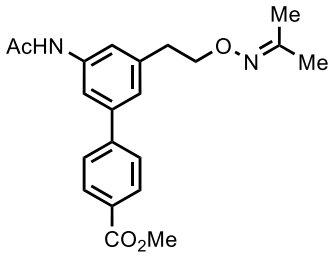
Methyl 3'-methoxy-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5c)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5c** was obtained as a pale-yellow liquid (51.6 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 6.99 (s, 1H), 6.82 (s, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.93 (s, 3H), 3.85 (s, 3H), 3.01 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.90, 159.99, 154.85, 145.55, 141.15, 129.95, 128.88, 127.00, 120.56, 114.30, 110.74, 73.62, 55.25, 52.04, 35.92, 21.81, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_4$ $[M+H]^+$ 342.1700, found 342.1697.



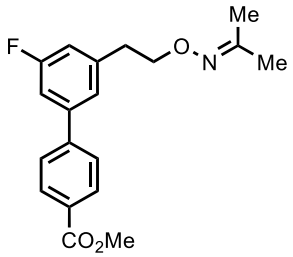
Methyl 3'-(2-((propan-2-ylideneamino)oxy)ethyl)-5'-(trifluoromethoxy)-[1,1'-biphenyl]-4-carboxylate (5d)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5d** was obtained as a white solid (46.2 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.31 (s, 1H), 7.13 (s, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.95 (s, 3H), 3.05 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.76, 155.20, 149.64 (q, *J* = 1.0 Hz), 144.11, 142.14, 141.79, 130.16, 129.50, 127.04, 126.34, 121.08, 120.48 (q, *J* = 256.0 Hz), 117.59, 73.11, 52.16, 35.60, 21.80, 15.56; ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{21}NO_4F_3$ $[M+H]^+$ 396.1417, found 396.1410.



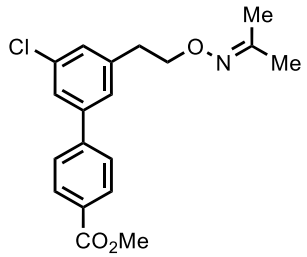
Methyl 3'-acetamido-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5e)

Upon purification by PTLC with PE/Et_2O (1/3) as the eluent, **5e** was obtained as a white solid (44.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.21 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.18 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.62, 166.99, 155.04, 145.18, 140.60, 140.58, 138.61, 129.93, 128.83, 126.96, 123.85, 120.09, 116.62, 73.49, 52.07, 35.77, 24.49, 21.77, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{25}N_2O_4$ $[M+H]^+$ 369.1809, found 369.1801.



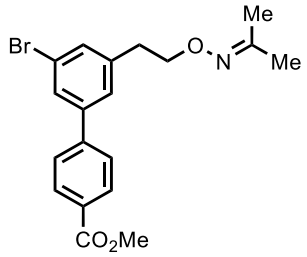
Methyl 3'-fluoro-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5f)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5f** was obtained as a white solid (40.9 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 3.02 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.77, 163.09 (d, *J* = 244.0 Hz), 155.07, 144.36 (d, *J* = 2.0 Hz), 142.22 (d, *J* = 7.0 Hz), 141.84 (d, *J* = 9.0 Hz), 130.08, 129.31, 126.95, 123.63 (d, *J* = 3.0 Hz), 115.50 (d, *J* = 21.0 Hz), 111.90 (d, *J* = 23.0 Hz), 73.21, 52.11, 35.60 (d, *J* = 2.0 Hz), 21.80, 15.62; ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.02 (t, *J* = 9.4 Hz); HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}NO_3F$ $[M+H]^+$ 330.1500, found 330.1497.



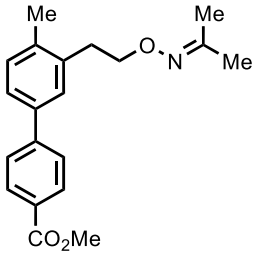
Methyl 3'-chloro-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5g)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **5g** was obtained as a white solid (48.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.35 (s, 1H), 7.24 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 3.00 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.74, 155.08, 144.22, 141.71, 141.58, 134.54, 130.09, 129.35, 128.73, 126.96, 126.22, 125.12, 73.18, 52.11, 35.51, 21.80, 15.62; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}NO_3Cl$ $[M+H]^+$ 346.1205, found 346.1205.



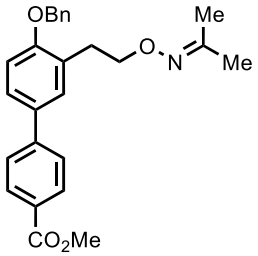
Methyl 3'-bromo-5'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5h)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5h** was obtained as a white solid (41.2 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.62–7.58 (m, 3H), 7.40 (s, 2H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 2.99 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.76, 155.15, 144.12, 141.95, 141.85, 131.67, 130.09, 129.34, 128.03, 126.98, 126.71, 122.77, 73.18, 52.13, 35.47, 21.82, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}NO_3Br$ $[M+H]^+$ 390.0699, found 390.0697.



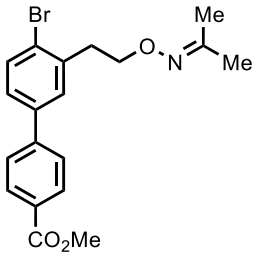
Methyl 4'-methyl-3'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5i)

5i was synthesized following the general *meta*-C–H arylation procedure using TFE as the solvent instead. Upon purification by PTLC with PE/EA (9/1) as the eluent, **5i** was obtained as a white solid (49.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99, 154.74, 145.56, 137.72, 137.50, 136.64, 130.72, 129.99, 128.50, 128.44, 126.69, 125.01, 72.83, 52.01, 33.13, 21.83, 19.14, 15.62; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$ 326.1751, found 326.1751.



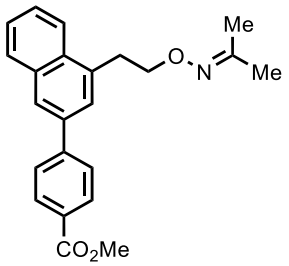
Methyl 4'-(benzyloxy)-3'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5j)

5j was synthesized following the general *meta*-C–H arylation procedure using TFE as the solvent instead. Upon purification by PTLC with PE/EA/DCM (15/1/2) as the eluent, **5j** was obtained as a white solid (49.0 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51–7.42 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.13 (s, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 3.11 (t, *J* = 6.8 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.01, 156.97, 154.61, 145.28, 137.03, 132.11, 130.00, 129.78, 128.52, 128.20, 128.09, 127.78, 126.98, 126.35, 126.14, 111.87, 72.41, 69.90, 51.99, 30.53, 21.82, 15.58; HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{28}NO_4$ $[M+H]^+$ 418.2013, found 418.2008.



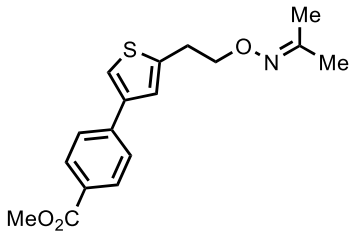
Methyl 4'-bromo-3'-(2-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5k)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5k** was obtained as a white solid (33.3 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.63–7.58 (m, 3H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.30 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 3.18 (t, *J* = 6.8 Hz, 2H), 1.88 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.82, 154.99, 144.44, 139.05, 138.97, 133.18, 130.12, 129.93, 129.10, 126.74, 126.56, 124.74, 71.93, 52.13, 36.00, 21.84, 15.65; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{21}NO_3Br$ $[M+H]^+$ 390.0699, found 390.0694.



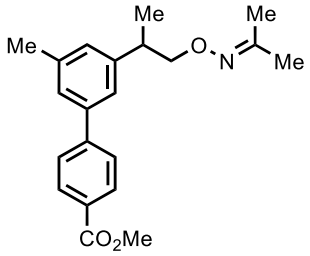
Methyl 4-(4-(2-((propan-2-ylideneamino)oxy)ethyl)naphthalen-2-yl)benzoate (5l)

5l was synthesized following the general *meta*-C–H arylation procedure using TFE as the solvent instead. Upon purification by PTLC with PE/EA (9/1) as the eluent, **5l** was obtained as a white solid (43.1 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) 8.16–8.09 (m, 3H), 7.96 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 1H), 7.56–7.46 (m, 2H), 4.41 (t, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 3.49 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.95, 154.91, 145.49, 136.73, 135.99, 133.99, 131.80, 130.08, 129.11, 128.83, 127.14, 126.34, 126.19, 126.10, 125.27, 123.86, 73.16, 52.07, 32.98, 21.85, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{24}NO_3$ $[M+H]^+$ 362.1751, found 362.1743.



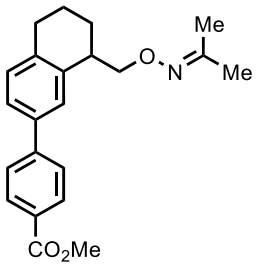
Methyl 4-(5-(2-((propan-2-ylideneamino)oxy)ethyl)thiophen-3-yl)benzoate (5m)

5m was synthesized following the general *meta*-C–H arylation procedure with 3.0 equiv. of AgOAc. Upon purification by PTLC with PE/EA (6/1) as the eluent, **5m** was obtained as a white solid (33.2 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.18 (s, 1H), 4.28 (t, *J* = 6.4 Hz, 2H), 3.92 (s, 3H), 3.20 (t, *J* = 6.4 Hz, 2H), 1.90 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.92, 155.35, 142.72, 140.59, 140.27, 130.14, 128.37, 125.95, 124.32, 120.33, 73.19, 52.07, 30.18, 21.87, 15.82; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}NO_3S$ $[M+H]^+$ 318.1158, found 318.1159.



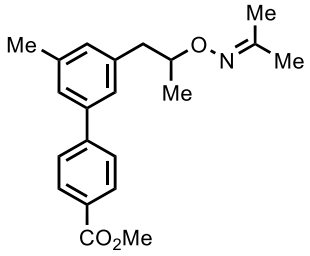
Methyl 3'-methyl-5'-(1-((propan-2-ylideneamino)oxy)propan-2-yl)-[1,1'-biphenyl]-4-carboxylate (5n)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **5n** was obtained as a colorless liquid (47.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 2H), 7.09 (s, 1H), 4.17 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.08 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.93 (s, 3H), 3.19 (sext, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 1.87 (s, 3H), 1.80 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 154.79, 145.95, 144.93, 139.89, 138.39, 129.94, 128.64, 128.06, 127.01, 126.05, 123.69, 78.60, 52.04, 39.26, 21.80, 21.49, 17.92, 15.58; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{26}NO_3$ $[M+H]^+$ 340.1907, found 340.1907.



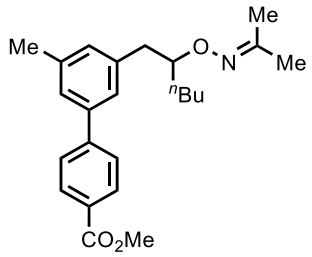
Methyl 4-(8-(((propan-2-ylideneamino)oxy)methyl)-5,6,7,8-tetrahydronaphthalen-2-yl)benzoate (5o)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5o** was obtained as a colorless liquid (47.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.38 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.28 (dd, *J* = 10.8, 5.6 Hz, 1H), 4.12 (dd, *J* = 10.8, 8.8 Hz, 1H), 3.93 (s, 3H), 3.28 (dq, *J* = 9.6, 4.8 Hz, 1H), 2.88–2.73 (m, 2H), 1.95–1.84 (m, 9H), 1.84–1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 154.75, 145.68, 137.95, 137.95, 137.12, 129.96, 129.69, 128.46, 128.13, 126.72, 124.74, 77.40, 52.00, 37.37, 29.44, 25.20, 21.85, 19.45, 15.69; HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{26}NO_3$ $[M+H]^+$ 352.1907, found 352.1901.



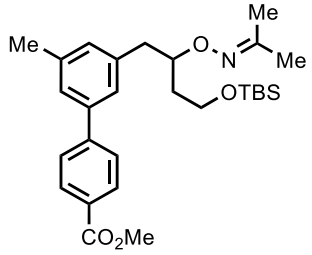
Methyl 3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)propyl)-[1,1'-biphenyl]-4-carboxylate (5p)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5p** was obtained as a colorless liquid (52.6 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 2H), 7.06 (s, 1H), 4.40 (sext, *J* = 6.4 Hz, 1H), 3.93 (s, 3H), 3.05 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.76 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.39 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H), 1.22 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 154.14, 145.85, 139.68, 139.41, 138.17, 130.28, 129.92, 128.59, 126.94, 125.72, 125.69, 78.79, 52.00, 41.99, 21.89, 21.38, 19.26, 15.69; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{26}NO_3$ $[M+H]^+$ 340.1907, found 340.1900.



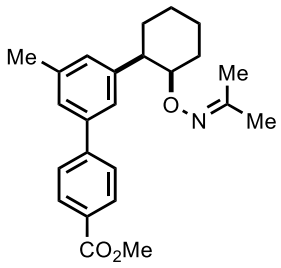
Methyl 3'-methyl-5'-(2-((propan-2-ylideneamino)oxy)hexyl)-[1,1'-biphenyl]-4-carboxylate (5q)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **5q** was obtained as a colorless liquid (66.5 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 2H), 7.05 (s, 1H), 4.26 (quin, *J* = 6.0 Hz, 1H), 3.93 (s, 3H), 3.01 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.83 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.38 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H), 1.65–1.38 (m, 3H), 1.37–1.24 (m, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.98, 153.90, 145.93, 139.67, 139.60, 138.08, 130.32, 129.91, 128.58, 126.93, 125.72, 125.61, 82.75, 52.00, 40.10, 32.68, 27.70, 22.71, 21.90, 21.39, 15.70, 14.04; HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{32}NO_3$ $[M+H]^+$ 382.2377, found 382.2372.



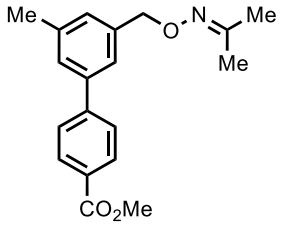
Methyl 3'-(4-((tert-butyldimethylsilyl)oxy)-2-((propan-2-ylideneamino)oxy)butyl)-5'-methyl-[1,1'-biphenyl]-4-carboxylate (5r)

Upon purification by PTLC with PE/EA (12/1) as the eluent, **5r** was obtained as a colorless liquid (78.9 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 2H), 7.06 (s, 1H), 4.42 (quin, *J* = 6.4 Hz, 1H), 3.94 (s, 3H), 3.79–3.65 (m, 2H), 3.07 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.88 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.39 (s, 3H), 1.93–1.75 (m, 8H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 154.00, 145.93, 139.66, 139.40, 138.12, 130.36, 129.90, 128.55, 126.95, 125.77, 125.68, 79.60, 59.97, 52.01, 40.34, 36.05, 25.90, 21.89, 21.39, 18.28, 15.67, -5.40; HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{42}NO_4Si$ $[M+H]^+$ 484.2878, found 484.2869.



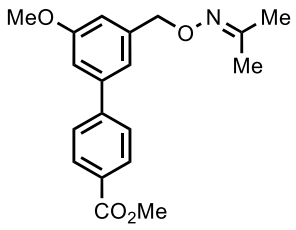
Methyl 3'-methyl-5'-(*cis*-2-((propan-2-ylideneamino)oxy)cyclohexyl)-[1,1'-biphenyl]-4-carboxylate (5s)

Upon purification by PTLC with PE/EA (10/1) as the eluent, **5s** was obtained as a colorless liquid (38.2 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.37 (s, 1H), 7.25 (s, 1H), 7.15 (s, 1H), 4.40 (s, 1H), 3.93 (s, 3H), 2.81 (dt, *J* = 12.8, 2.8 Hz, 1H), 2.38 (s, 3H), 2.23 (d, *J* = 12.4 Hz, 1H), 2.10 (qd, *J* = 12.8, 3.6 Hz, 1H), 1.92–1.81 (m, 4H), 1.80–1.69 (m, 4H), 1.63–1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.05, 153.83, 146.27, 145.30, 139.33, 137.74, 129.89, 129.14, 128.47, 126.95, 125.68, 124.47, 80.08, 52.01, 47.38, 30.58, 27.02, 26.32, 21.80, 21.51, 19.96, 15.63; HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{30}NO_3$ $[M+H]^+$ 380.2220, found 380.2211.



Methyl 3'-methyl-5'-(((propan-2-ylideneamino)oxy)methyl)-[1,1'-biphenyl]-4-carboxylate (5t)

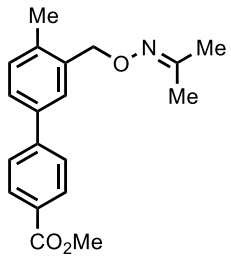
Upon purification by PTLC with PE/EA (9/1) as the eluent, **5t** was obtained as a colorless liquid (49.0 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.36 (s, 1H), 7.21 (s, 1H), 5.09 (s, 2H), 3.94 (s, 3H), 2.43 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 155.39, 145.67, 140.01, 138.92, 138.60, 129.99, 128.75, 128.48, 127.37, 127.05, 124.03, 75.11, 52.09, 21.89, 21.46, 15.82; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found: 312.1588.



Methyl 3'-methoxy-5'-(((propan-2-ylideneamino)oxy)methyl)-[1,1'-biphenyl]-4-carboxylate (5u)

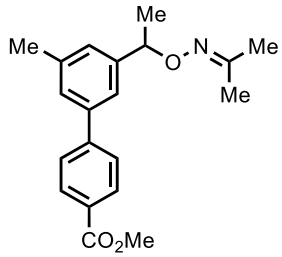
Upon purification by PTLC with PE/EA (9/1) as the eluent, **5u** was obtained as a pale-yellow liquid (51.9 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 7.06 (s, 1H), 6.95 (s, 1H), 5.10 (s, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 166.87, 160.03, 155.41, 145.39, 141.33, 140.58, 129.96, 128.95, 127.04, 119.11, 112.85, 112.17, 74.91, 55.31, 52.03, 21.81, 15.75; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_4$ $[M+H]^+$: 328.1543, found: 328.1535.



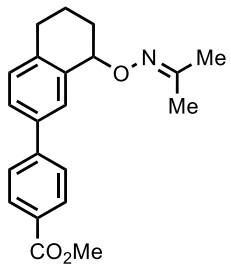
Methyl 4'-methyl-3'-(((propan-2-ylideneamino)oxy)methyl)-[1,1'-biphenyl]-4-carboxylate (5v)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5v** was obtained as a colorless liquid (49.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.13 (s, 2H), 3.92 (s, 3H), 2.40 (s, 3H), 1.89 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.95, 155.24, 145.43, 137.37, 136.97, 136.57, 130.72, 129.99, 128.53, 127.63, 126.73, 126.47, 73.58, 52.00, 21.83, 18.64, 15.64; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found: 312.1593.



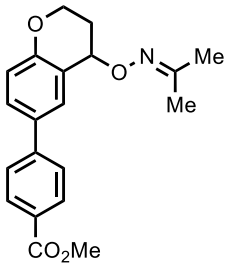
Methyl 3'-methyl-5'-(1-((propan-2-ylideneamino)oxy)ethyl)-[1,1'-biphenyl]-4-carboxylate (5w)

Upon purification by PTLC with PE/EA (9/1) as the eluent, **5w** was obtained as a pale-yellow liquid (50.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.32 (s, 1H), 7.16 (s, 1H), 5.22 (q, *J* = 6.4 Hz, 1H), 3.93 (s, 3H), 2.42 (s, 3H), 1.93 (s, 3H), 1.84 (s, 3H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 154.83, 145.85, 144.75, 139.88, 138.44, 129.94, 128.65, 127.02, 126.95, 126.62, 122.17, 80.04, 52.03, 22.50, 21.89, 21.51, 15.85; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$: 326.1751, found: 326.1752.



Methyl 4-(8-((propan-2-ylideneamino)oxy)-5,6,7,8-tetrahydronaphthalen-2-yl)benzoate (5x)

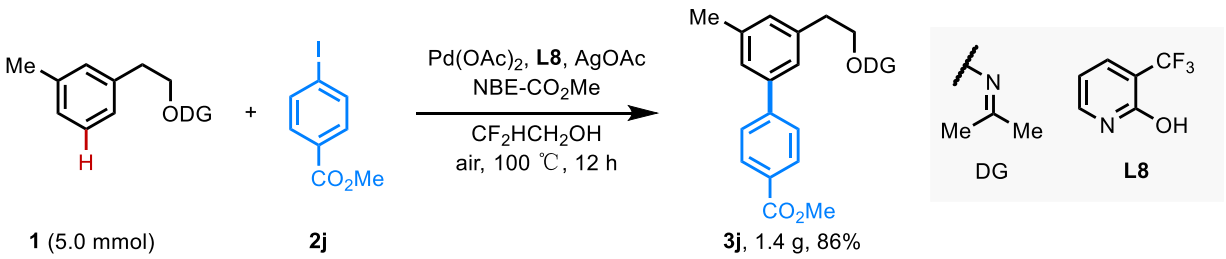
5x was synthesized following the general *meta*-C–H arylation procedure using **L14** as the ligand. Upon purification by PTLC with PE/EA/DCM (10/1/1) as the eluent, **5x** was obtained as a white solid (55.7 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.21 (t, *J* = 4.0 Hz, 1H), 3.92 (s, 3H), 2.88 (dt, *J* = 16.4, 4.4 Hz, 1H), 2.81–2.71 (m, 1H), 2.20–2.11 (m, 1H), 2.02–1.93 (m, 2H), 1.92 (s, 3H), 1.85 (s, 3H), 1.82–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 154.88, 145.48, 138.25, 137.33, 136.19, 129.97, 129.44, 128.83, 128.48, 126.76, 126.36, 76.68, 52.01, 29.10, 28.73, 21.94, 18.52, 15.94; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{24}NO_3$ $[M+H]^+$: 338.1751, found: 338.1749.



methyl 4-(4-((propan-2-ylideneamino)oxy)chroman-6-yl)benzoate (5y)

5y was synthesized following the general *meta*-C–H arylation procedure using **L14** as the ligand. Upon purification by PTLC with PE/EA (9/1) as the eluent, **5y** was obtained as a white solid (38.5 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 1H), 4.34–4.19 (m, 2H), 3.93 (s, 3H), 2.31 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.20–2.09 (m, 1H), 1.92 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.03, 155.68, 155.63, 145.13, 131.87, 130.11, 130.03, 128.52, 128.15, 126.40, 121.43, 117.45, 72.74, 62.35, 52.02, 27.87, 21.95, 16.02; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{22}NO_4$ $[M+H]^+$: 340.1543, found: 340.1537.

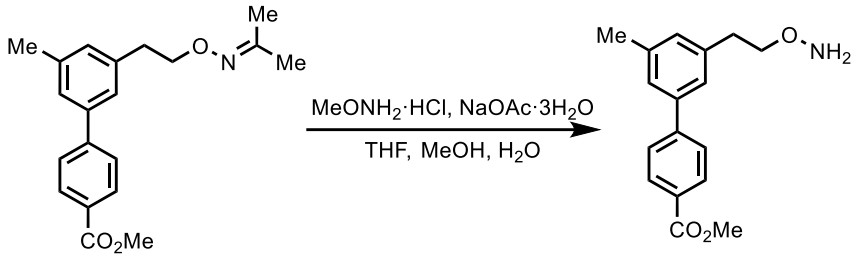
2.5 Gram-Scale Reaction



1 (5.0 mmol) **2j** **3j**, 1.4 g, 86%

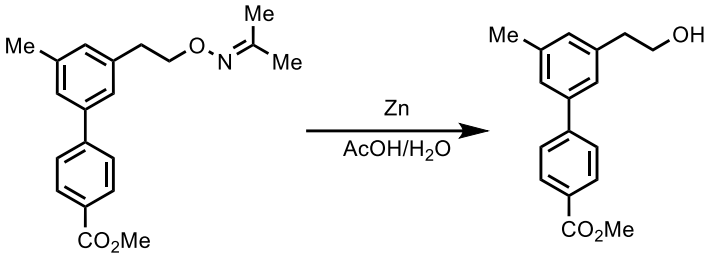
To a 100 mL sealed tube were added $Pd(OAc)_2$ (112.4 mg, 0.5 mmol), **L8** (163.4 mg, 1.0 mmol), AgOAc (1.25 g, 7.5 mmol), methyl 4-iodobenzoate (**2j**, 2.62 g, 10.0 mmol), CF_2HCH_2OH (5.0 mL), propan-2-one *O*-(3-methylphenethyl) oxime (**1**, 0.99 mL, 5.0 mmol) and NBE-CO_2Me (0.90 mL, 7.5 mmol). The tube was capped and closed tightly. Then the reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with DCM, filtered through a pad of celite and washed with DCM. The resulting solution was concentrated and purified by column chromatography on silica gel with PE/EA/DCM (15/1/1 to 10/1/1) to afford **3j** as a white solid (1.4 g, 86%).

2.6 Removal of the Directing Group



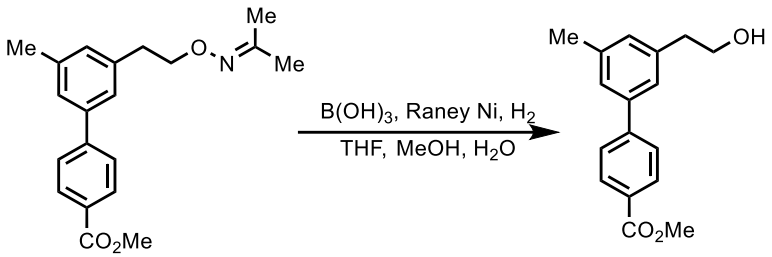
3j **6**

To a 100 mL round-bottomed flask were added **3j** (32.5 mg, 0.1 mmol), $MeONH_2$·HCl (0.21 g, 2.5 mmol), $NaOAc·3H_2O$ (64.1 mg, 0.5 mmol), MeOH (1.0 mL), H_2O (1.0 mL) and THF (1.0 mL). The reaction mixture was stirred at room temperature for 7.5 h, then another $MeONH_2$·HCl (0.10 g, 1.3 mmol) and $NaOAc·3H_2O$ (39.4 mg, 0.3 mmol) were added and the reaction mixture was stirred at room temperature for 40 min. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with dichloromethane (3 times). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude residue was purified by PTLC with PE/EA (4/1) to afford **6** as a white solid (28.6 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 2H), 7.07 (s, 1H), 5.35 (br s, 2H), 3.97–3.89 (m, 5H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99, 145.72, 140.08, 139.45, 138.59, 129.95, 129.47, 128.70, 127.02, 126.04, 124.95, 76.34, 52.05, 34.94, 21.40; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}NO_3$ $[M+H]^+$: 286.1438, found: 286.1434.



3j **7**

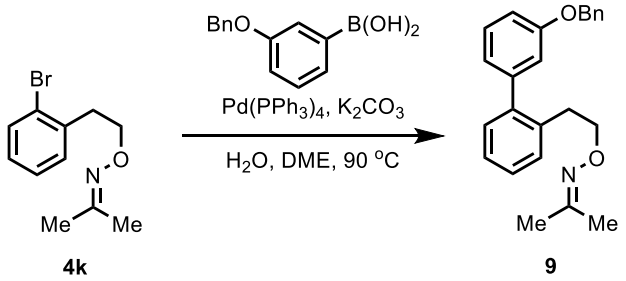
To a 100 mL round-bottomed flask were added **3j** (32.5 mg, 0.1 mmol), Zn dust (0.13 g, 2.0 mmol), AcOH (3.0 mL) and H_2O (3.0 mL). The reaction mixture was sonicated for 4.0 h, then Zn dust (68 mg, 1.0 mmol) was added and the reaction mixture was sonicated for 2.0 h, then Zn dust (66 mg, 1.0 mmol) was added and the reaction mixture was sonicated for another 2.0 h. After most of the starting material was consumed (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 times). The combined organic phases were washed with H_2O, saturated $NaHCO_3$ solution and saturated NaCl solution successively, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by PTLC with PE/EA (5/1) to afford **7** as a white solid (21.7 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.28 (s, 1H), 7.08 (s, 1H), 3.93 (s, 3H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 1.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.01, 145.61, 140.25, 139.17, 138.80, 129.98, 129.61, 128.75, 127.02, 126.24, 125.09, 63.58, 52.09, 39.08, 21.40; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1329, found: 271.1324.



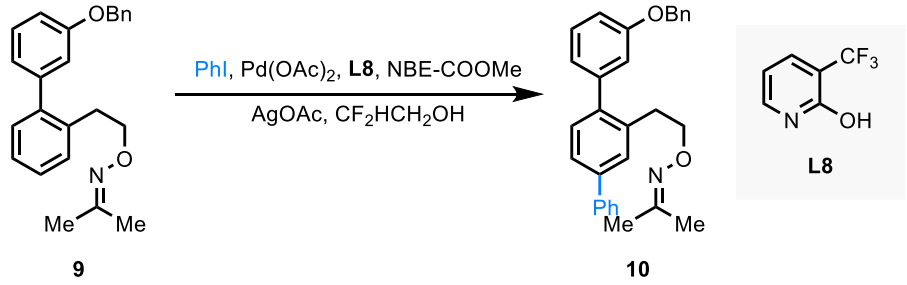
3j **7**

To a 250 mL round-bottomed flask were added (0.33 g, 1.0 mmol), $B(OH)_3$ (0.26 g, 4.3 mmol), H_2O (5.0 mL), MeOH (20 mL), THF (20 mL), Raney Ni (~3 mL, 50 μm dispersed in H_2O). The reaction mixture was vacuumed and backfilled with H_2 (3 times), then it was stirred for 24 h at room temperature under H_2 atmosphere. The mixture was diluted with EA and filtered through a pad of celite. The eluent was washed with water and saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA (4/1) to provide **7** as a white solid (0.26 g, 95%). The characterizing data was the same as above.

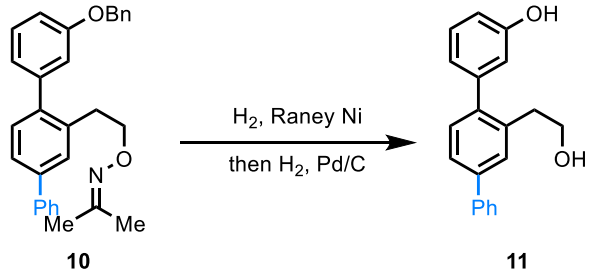
2.7 Synthesis of 11 and 12



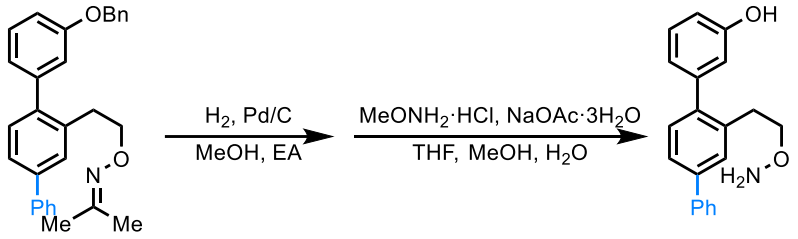
To a 100 mL sealed tube were added $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), 3-$BnOC_6H_4B(OH)_2$ (1.1 g, 4.8 mmol), DME (20 mL) and **4k** (1.0 g, 3.9 mmol). Then a solution of K_2CO_3 (1.6 g, 11.6 mmol) in H_2O (6.0 mL) was added while stirring. The tube was sealed and heated to 90 °C for 48 h. Then it was cooled to room temperature, diluted with H_2O and extracted with ethyl acetate (2 times). The combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA/DCM (20/1/1) to provide **9** as a white solid (1.3 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.41–7.19 (m, 8H), 6.99–6.90 (m, 3H), 5.08 (s, 2H), 4.10 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 1.82 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.44, 154.57, 143.08, 142.08, 136.94, 136.20, 129.91, 129.90, 129.07, 128.53, 127.90, 127.46, 127.29, 125.98, 122.05, 115.74, 113.42, 73.57, 69.95, 32.59, 21.82, 15.66; HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$: 360.1958, found: 360.1957.



To an 8.0 mL vial were added $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), **L8** (13.0 mg, 0.08 mmol), AgOAc (100.1 mg, 0.6 mmol), **9** (71.9 mg, 0.2 mmol), CF_2HCH_2OH (0.4 mL), PhI (89.5 μL, 0.8 mmol) and NBE-COOMe (72 μL, 0.6 mmol). The vial was capped and closed tightly. Then the reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with DCM, filtered through silica and washed with DCM. The resulting solution was concentrated and purified by column chromatography on silica gel with PE/EA/DCM (20/1/1) to afford a mixture of **10** with a small amount of **9** as a colorless liquid (70.2 mg).



To a 100 mL round-bottomed flask were added crude **10** (70.2 mg), $B(OH)_3$ (43.3 mg, 0.7 mmol), H_2O (1.0 mL), MeOH (4.0 mL), THF (4.0 mL), Raney Ni (about 1.0 mL, 50 μm dispersed in H_2O). The reaction mixture was vacuumed and backfilled with H_2 (3 times), then it was stirred for 23 h at room temperature under H_2 atmosphere. The mixture was diluted with ethyl acetate and filtered through a pad of celite. The eluent was washed with water and saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was dissolved in MeOH (2.0 mL), then 10% Pd/C (18 mg) was added. The reaction mixture was vacuumed and backfilled with H_2 (3 times), then it was stirred for 22 h at room temperature under H_2 atmosphere. The mixture was filtered through a pad of celite and washed with ethyl acetate. The solvent was evaporated and the crude residue was purified by column chromatography on silica gel with DCM/EA (5/1) to afford **11** as a white solid (38.3 mg, 66% from **9**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.55 (s, 1H), 7.53–7.42 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.33–7.28 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.87–6.81 (m, 2H), 5.39 (brs, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 1.26 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.46, 142.68, 141.13, 140.63, 140.47, 135.90, 130.67, 129.54, 128.80, 128.49, 127.39, 127.08, 125.14, 121.69, 116.33, 114.11, 63.45, 36.13; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1199, found: 313.1194.

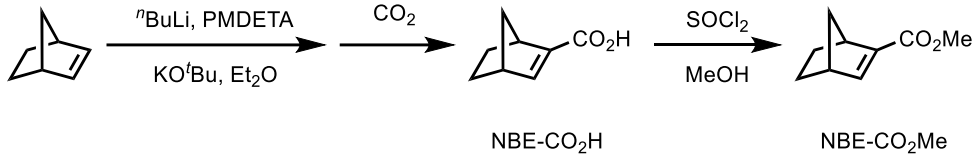


10 **12**

To a 100 mL round-bottomed flask were added **10** (68.2 mg), ethyl acetate (2.0 mL) and MeOH (5.0 mL). Then 10% Pd/C (7.4 mg) was added, and the reaction mixture was vacuumed and backfilled with H_2 (3 times) and stirred for 96 h at room temperature under H_2 atmosphere. The mixture was filtered through a pad of celite and washed with ethyl acetate. The solvent was evaporated, and the crude residue was used without purification.

The crude product was dissolved in mixed solvent (4.5 mL, THF/MeOH /H_2O = 1/1/1). Then $MeONH_2$·HCl (0.40 g, 5.0 mmol) and NaOAc·$3H_2O$ (0.4 g, 3.0 mmol) were added and the reaction mixture was stirred at room temperature for 4.0 h. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 times). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with DCM/EA (5/1) to afford **12** as a white solid (38.6 mg, 63% from **9**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.52 (s, 1H), 7.49–7.41 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.30–7.23 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.85 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.23 (brs, 3H), 3.84 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.52, 142.71, 140.97, 140.68, 140.36, 136.14, 130.50, 129.52, 128.75, 128.52, 127.31, 127.08, 125.01, 121.58, 116.36, 114.13, 32.03; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found: 306.1487.

2.8 Synthesis of NBE-CO_2Me



The procedure was modified according to the literature[7]. KO^{t}Bu (11.1 g, 99 mmol) was added to a 1 L 2-necked round-bottomed flask, then it was vacuumed and back filled with N_2 (3 times). Then Et_2O (100 mL) and *N*,*N*,*N'*,*N'*,*N''*-pentamethyldiethylenetriamine (PMDETA, 42 mL, 201 mmol) was added. The mixture was cooled to -78 °C and norbornene (9.8 g, 105 mmol) was added while stirring. Then ^{n}BuLi (83.3 mL, 2.4 M in hexane, 200 mmol) was added dropwise. Upon completion, the reaction was allowed to warm to room temperature and stirred for 1.0 h. Then the mixture was cooled to -78 °C and dry ice (the surface was washed with petroleum ether prior to use) was added until no gas was generated obviously. The reaction was stirred for 2.0 h at -78 °C and then slowly warm to room temperature. Then it was quenched by adding 4M HCl carefully and acidified with concentrated HCl until pH < 1 (usually all the solids are dissolved). The mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with PE/EA (4/1 to 3/1) to provide NBE-CO_2H as a yellow oil (5.8 g, 40%).

To a stirred solution of NBE-CO_2H (5.8 g, 42 mmol) in MeOH (85 mL) was added $SOCl_2$ (9.0 mL, 124 mmol) dropwise. The reaction was stirred for 1.5 h, quenched with saturated Na_2CO_3 solution and extracted with Et_2O (3 times). The combined organic layers were washed with saturated Na_2CO_3 solution twice and saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel with ^{n}Pentane/Et_2O (20/1) to provide NBE-CO_2Me as a pale-yellow liquid (4.8 g, 75%).

3. References

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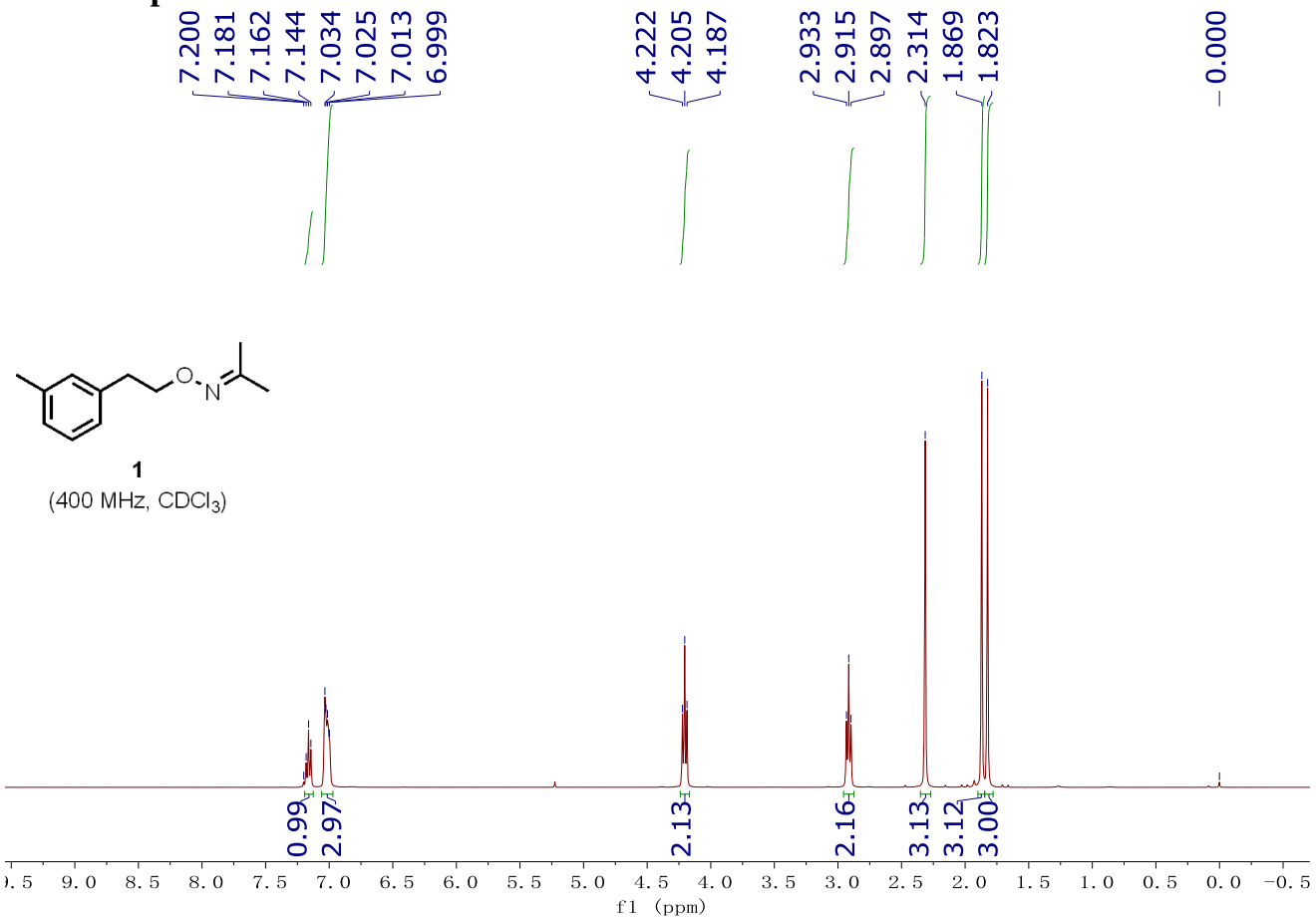
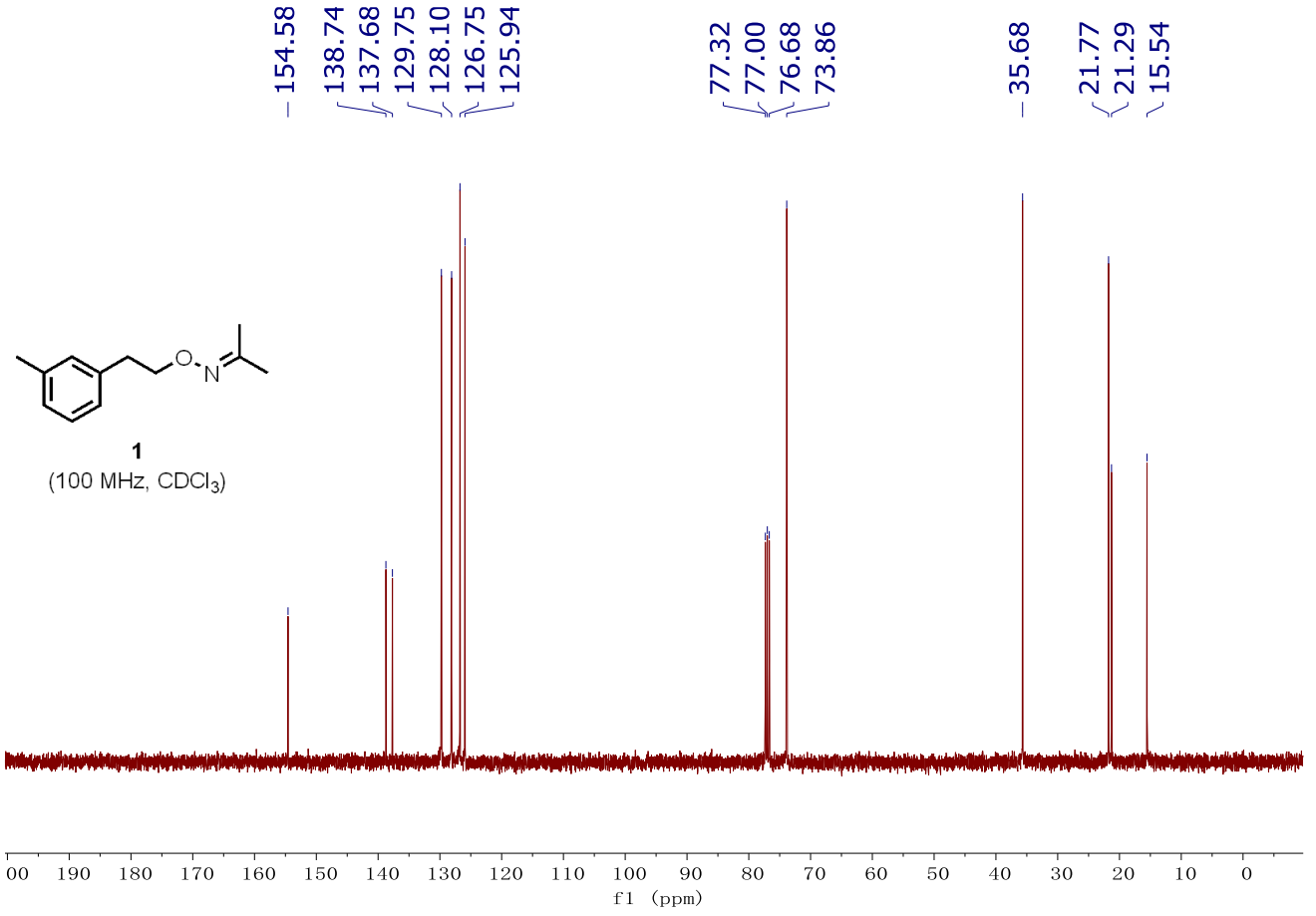
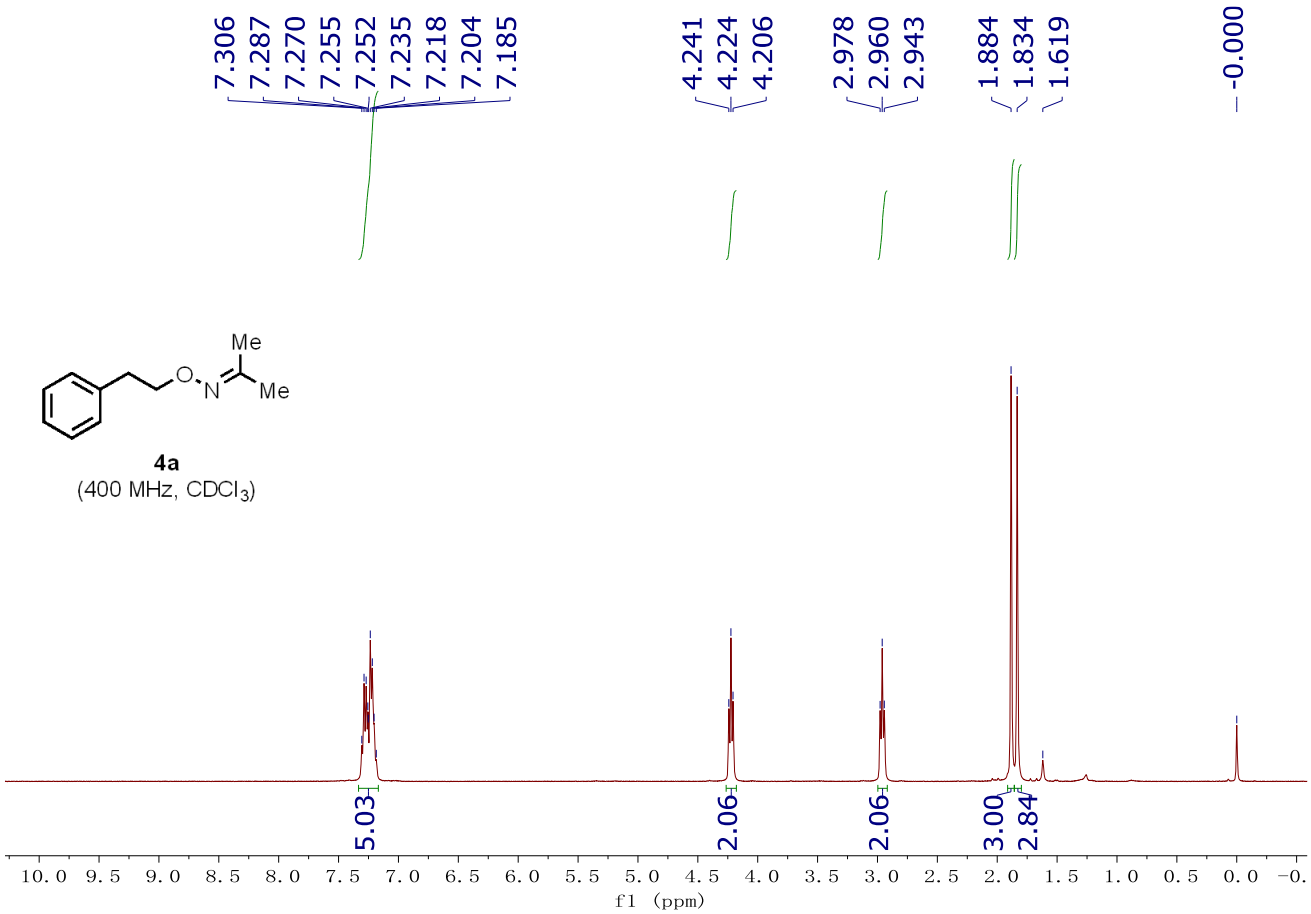
[6] K. Guo, X. Chen, J. Zhang, Y. Zhao, *Chem. Eur. J.* **2015**, *21*, 17474.

[7] Y. Wang, J. Liu, L. Huang, R. Zhu, X. Huang, R. Moird, J. Huang, *Chem. Commun.* **2017**, *53*, 4589.

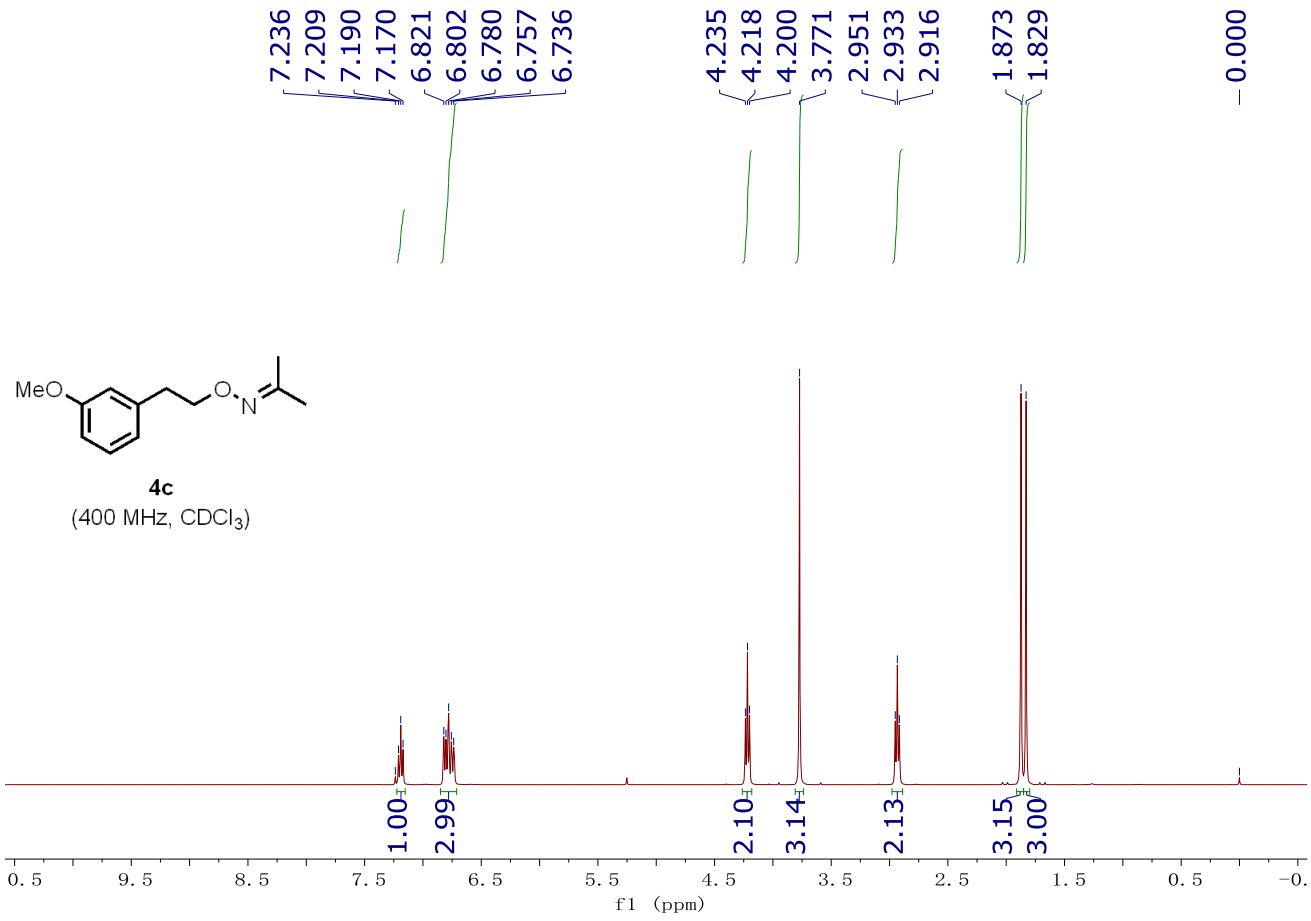
4. NMR Spectra



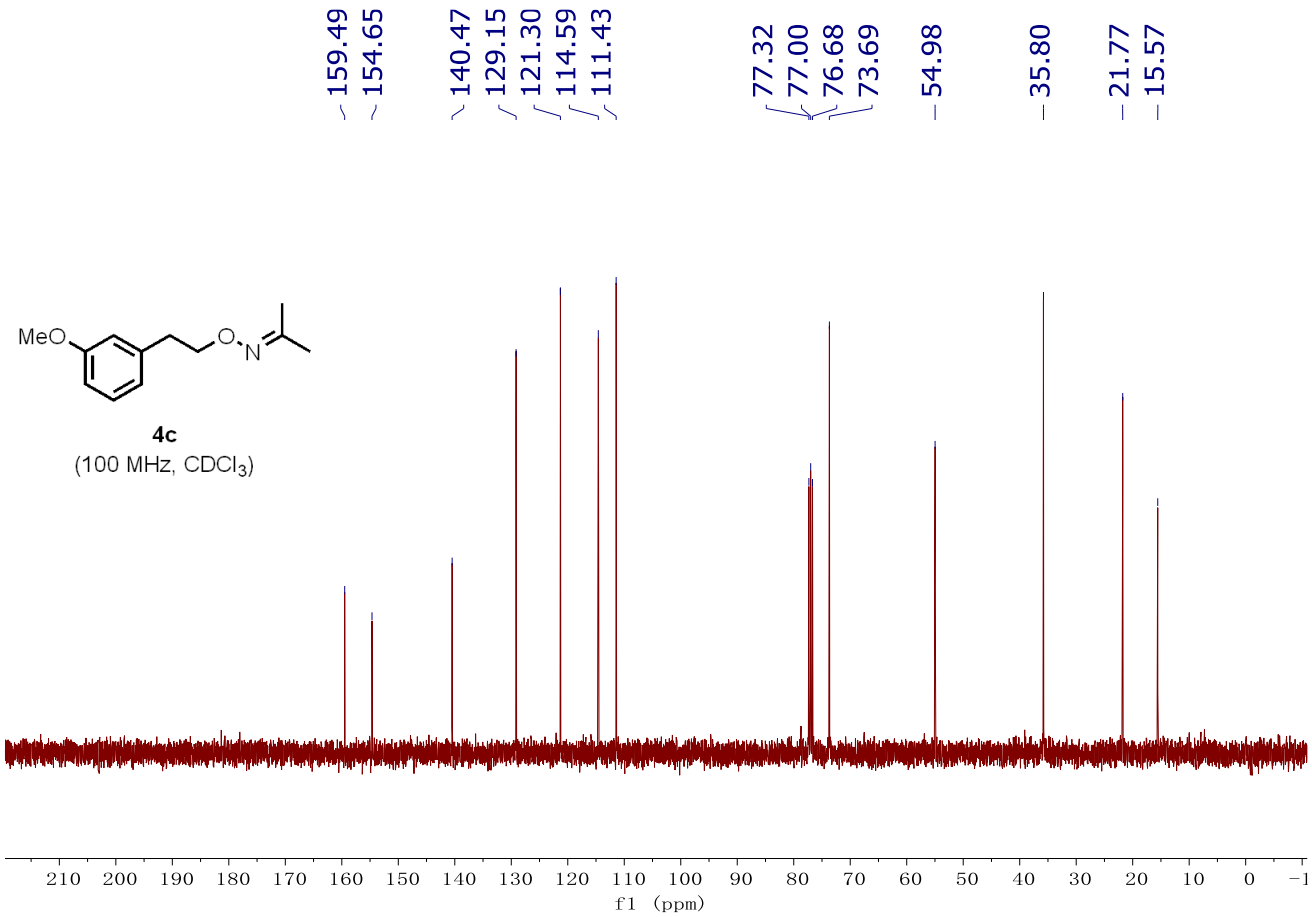




4a
(400 MHz, $CDCl_3$)



4c
(400 MHz, $CDCl_3$)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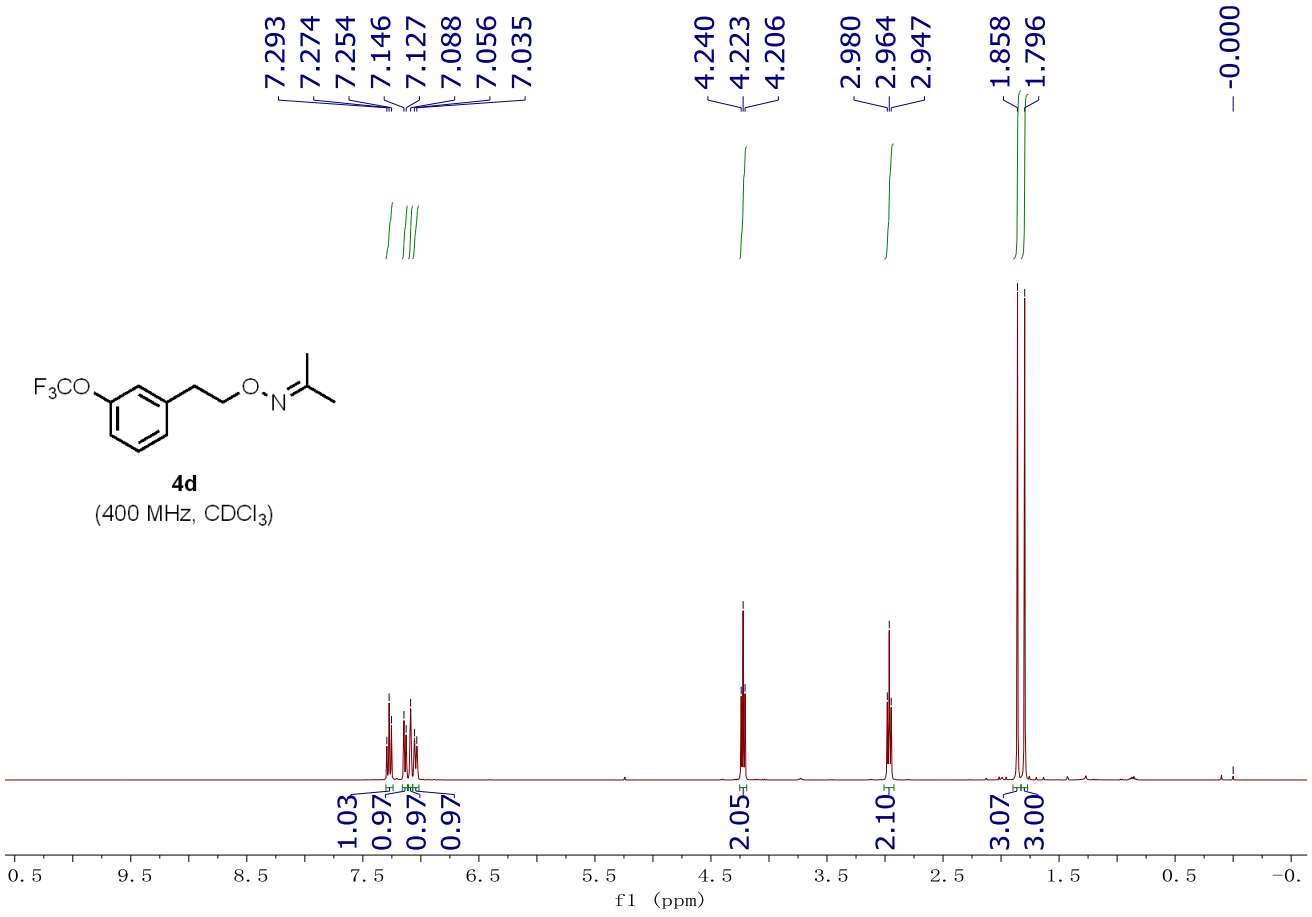
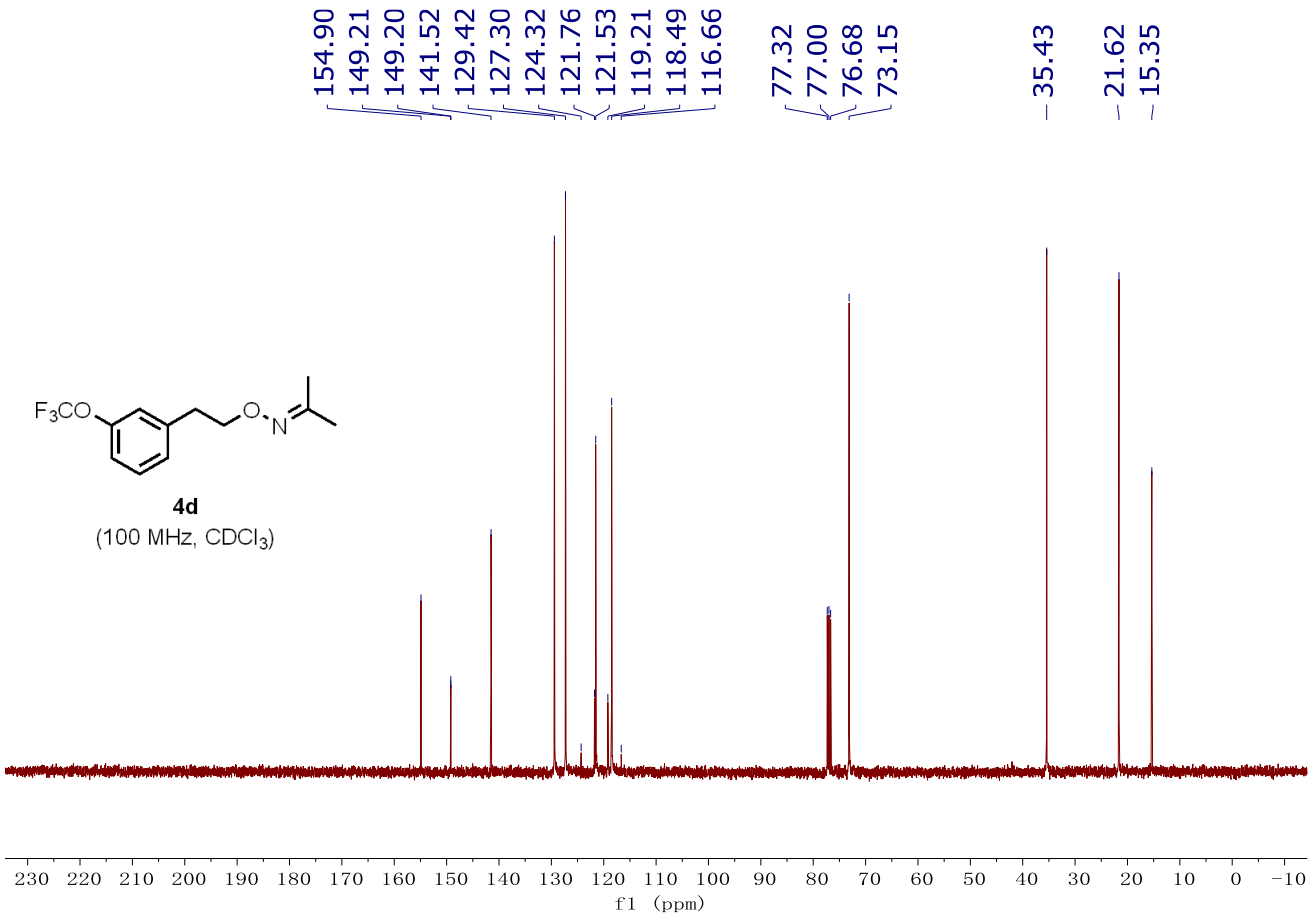
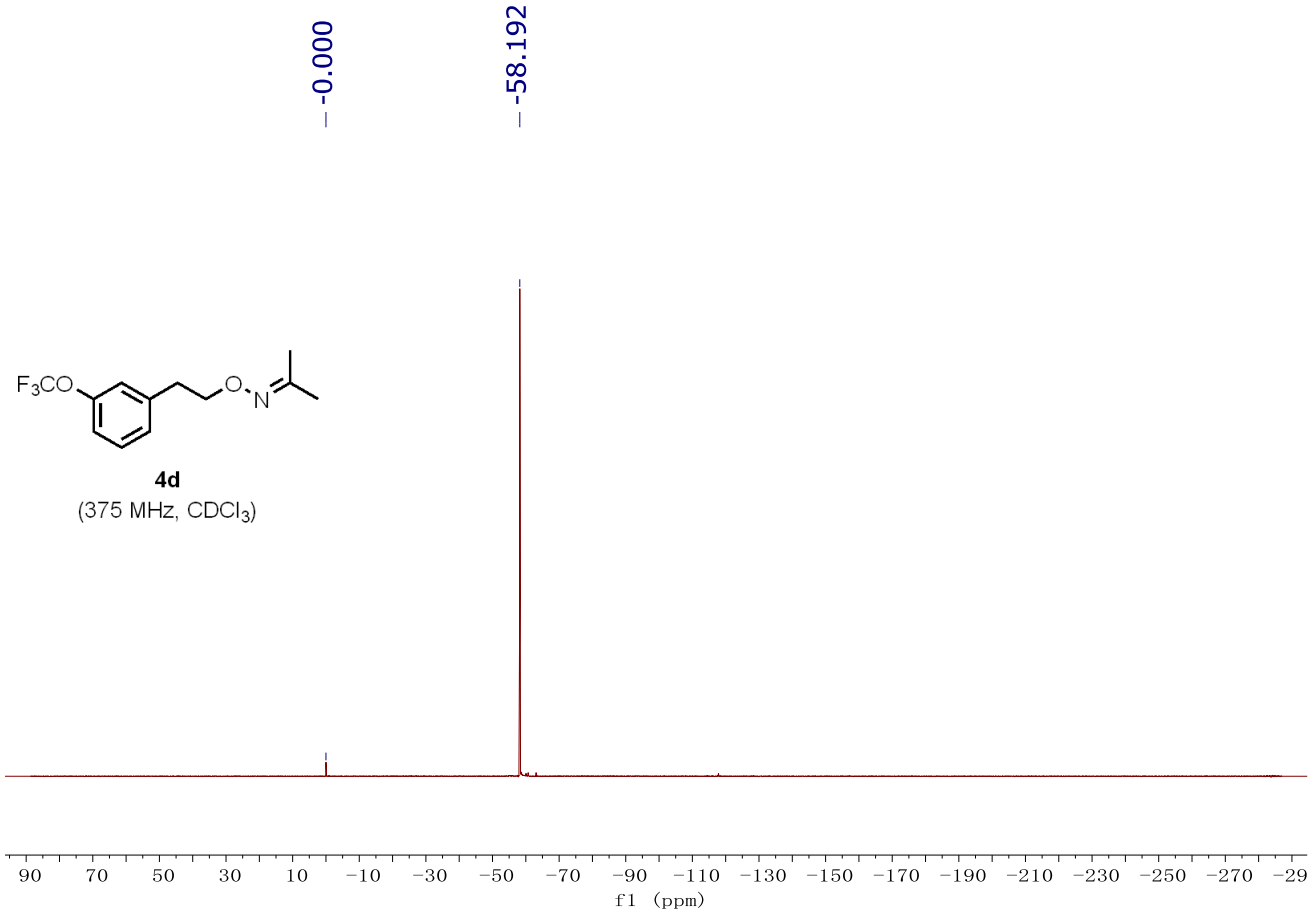
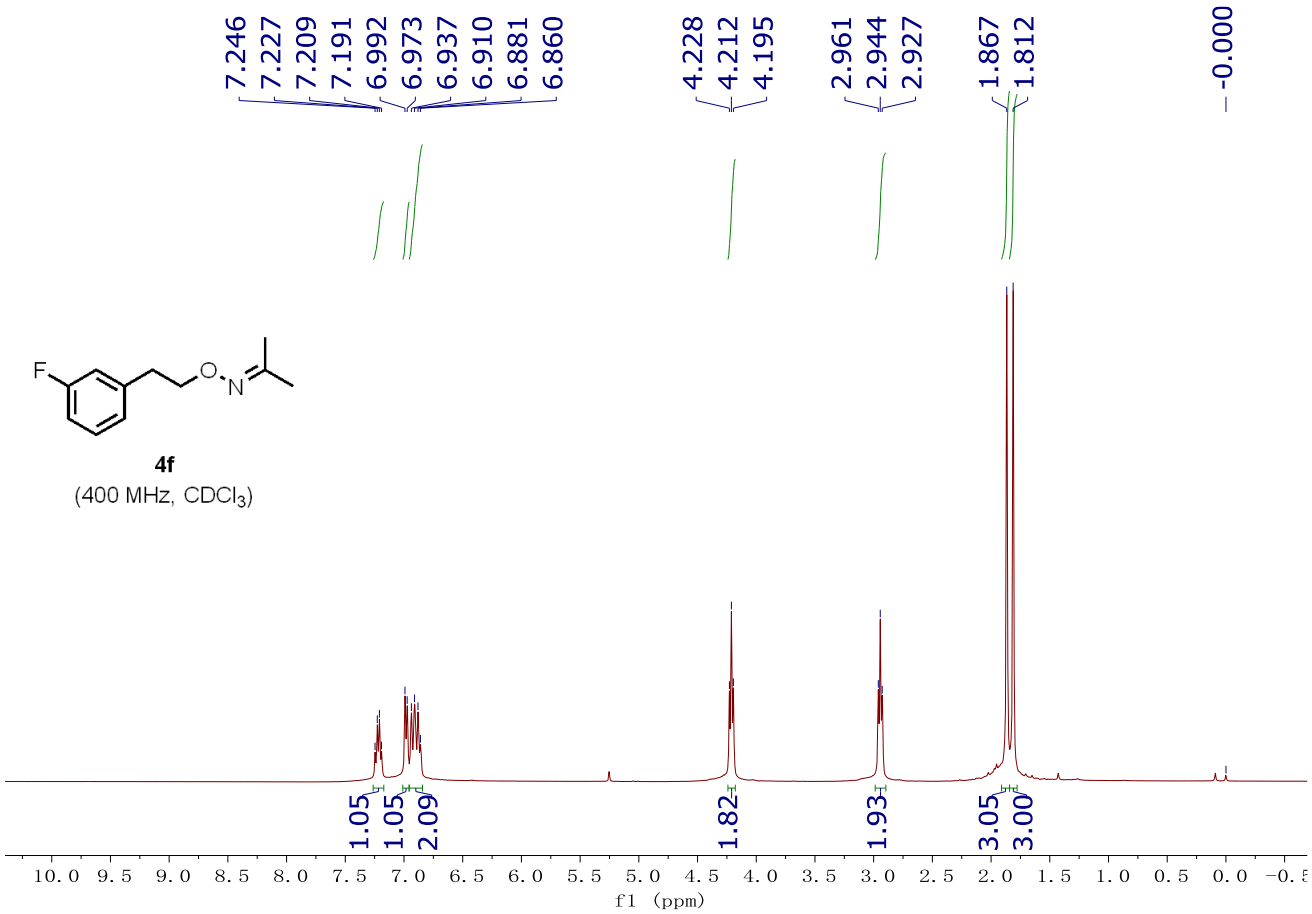
154.65
140.47
129.15
121.30
114.59
111.43
77.32
77.00
76.68
73.69
54.98
35.80
21.77
15.57
MeO
O
N
4c
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

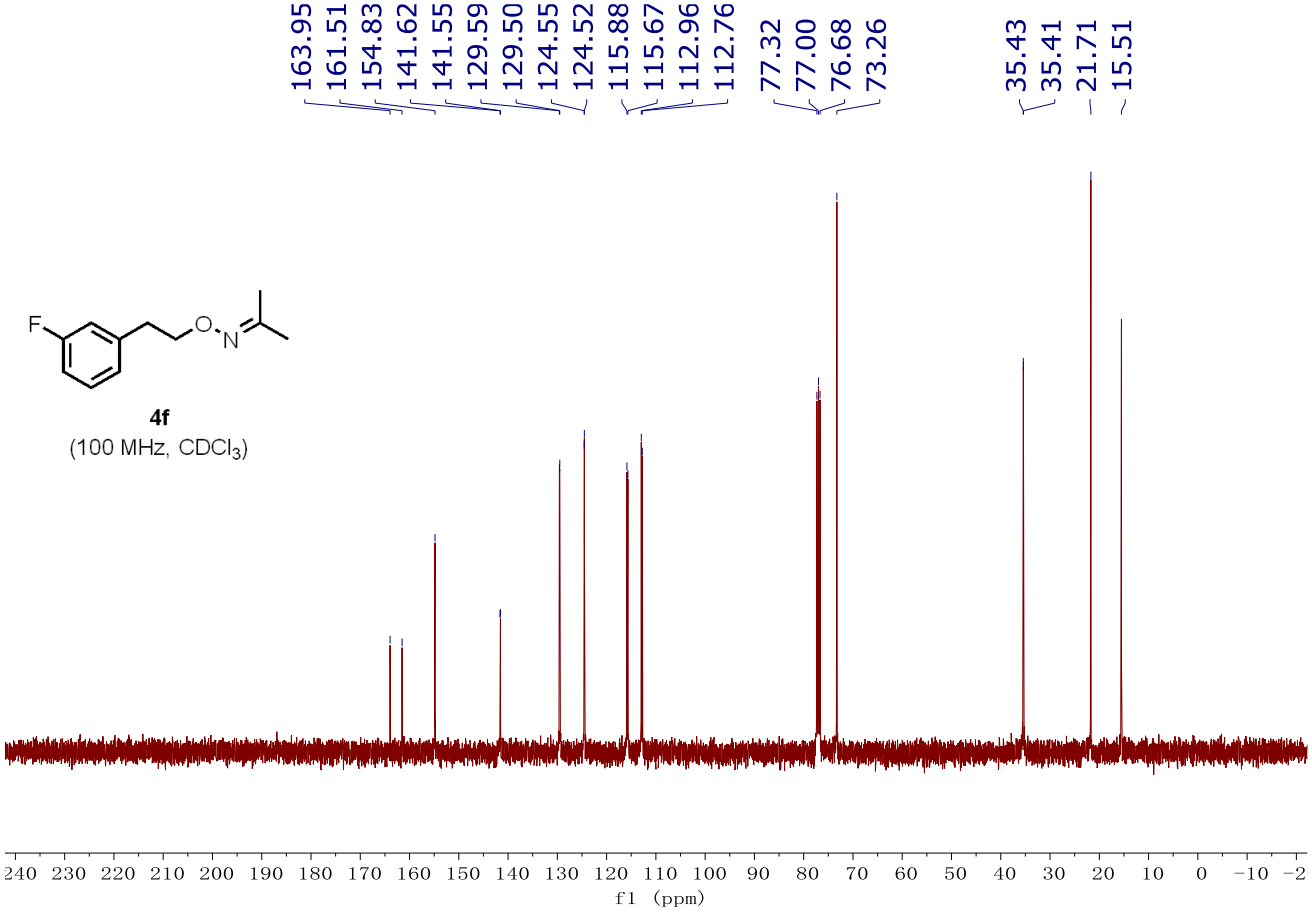

7.293
7.274
7.254
7.146
7.127
7.088
7.056
7.035
4.240
4.223
4.206
2.980
2.964
2.947
1.858
1.796
-0.000
F3CO
O
N
4d
(400 MHz, CDCl3)
1.03
0.97
0.97
0.97
2.05
2.10
3.07
3.00
0.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.
f1 (ppm)


154.90
149.21
149.20
141.52
129.42
127.30
124.32
121.76
121.53
119.21
118.49
116.66
77.32
77.00
76.68
73.15
35.43
21.62
15.35
F3CO
O
N
4d
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

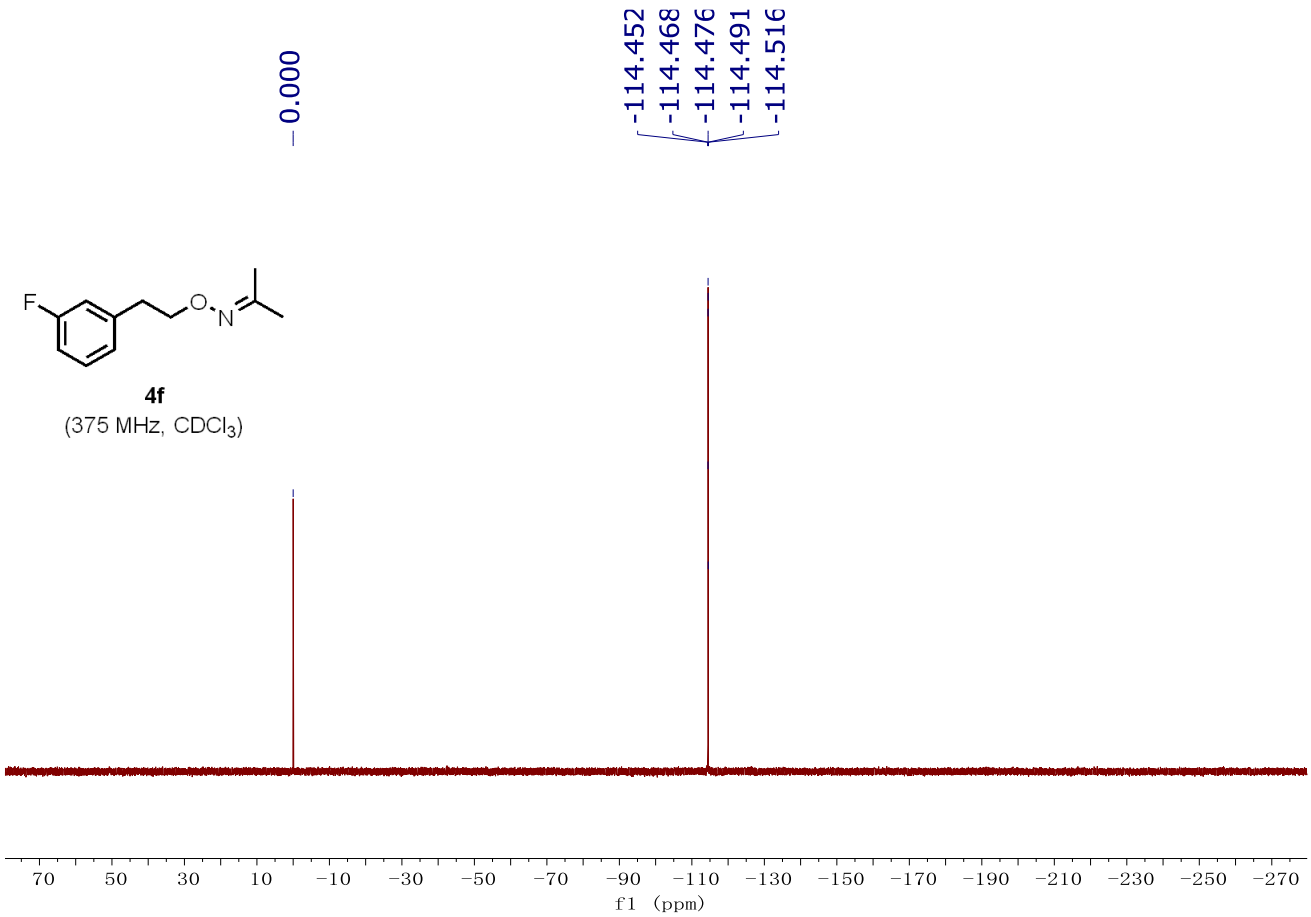

-0.000
-58.192
F3CO
O
N
4d
(375 MHz, CDCl3)
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −29
f1 (ppm)

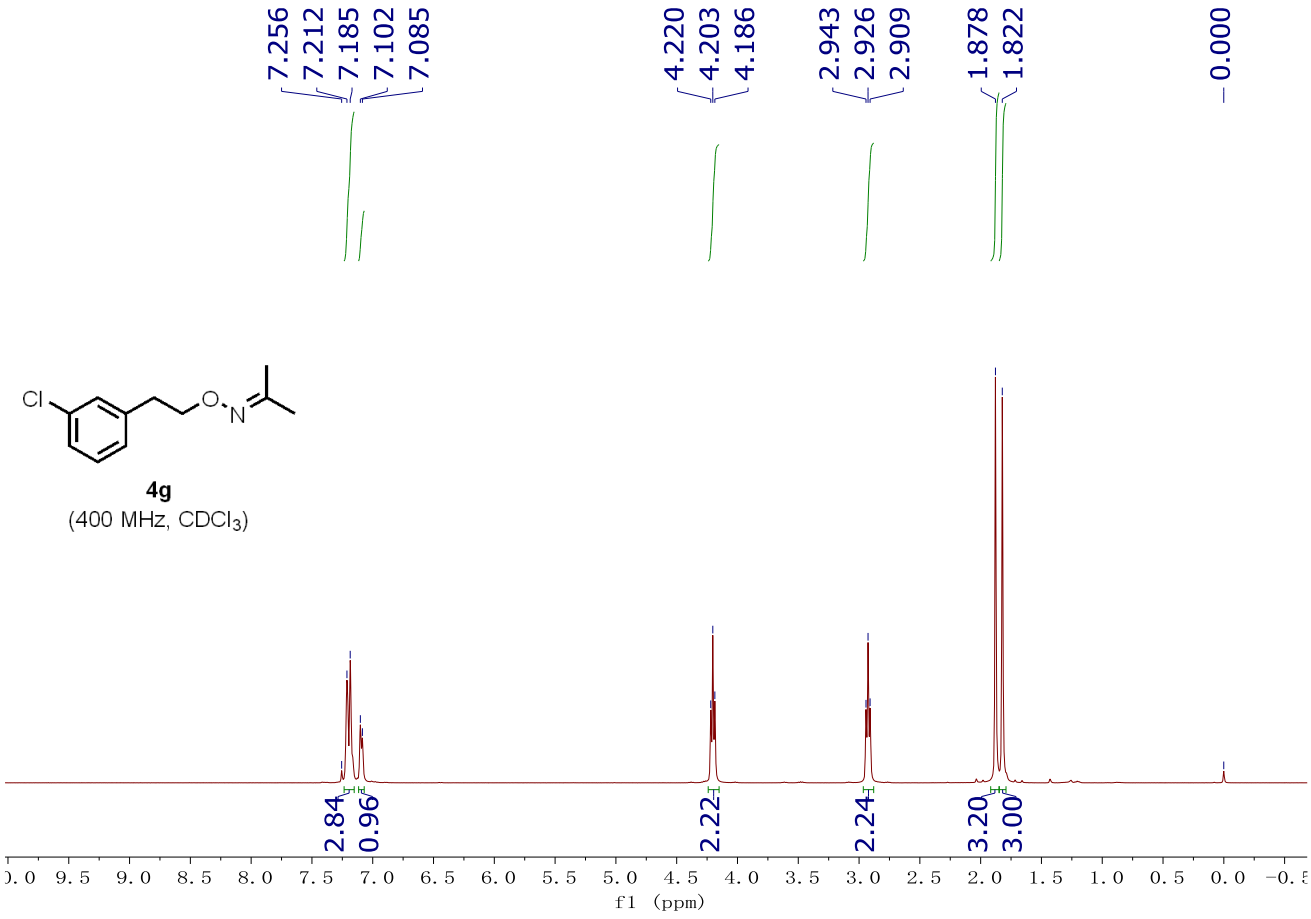


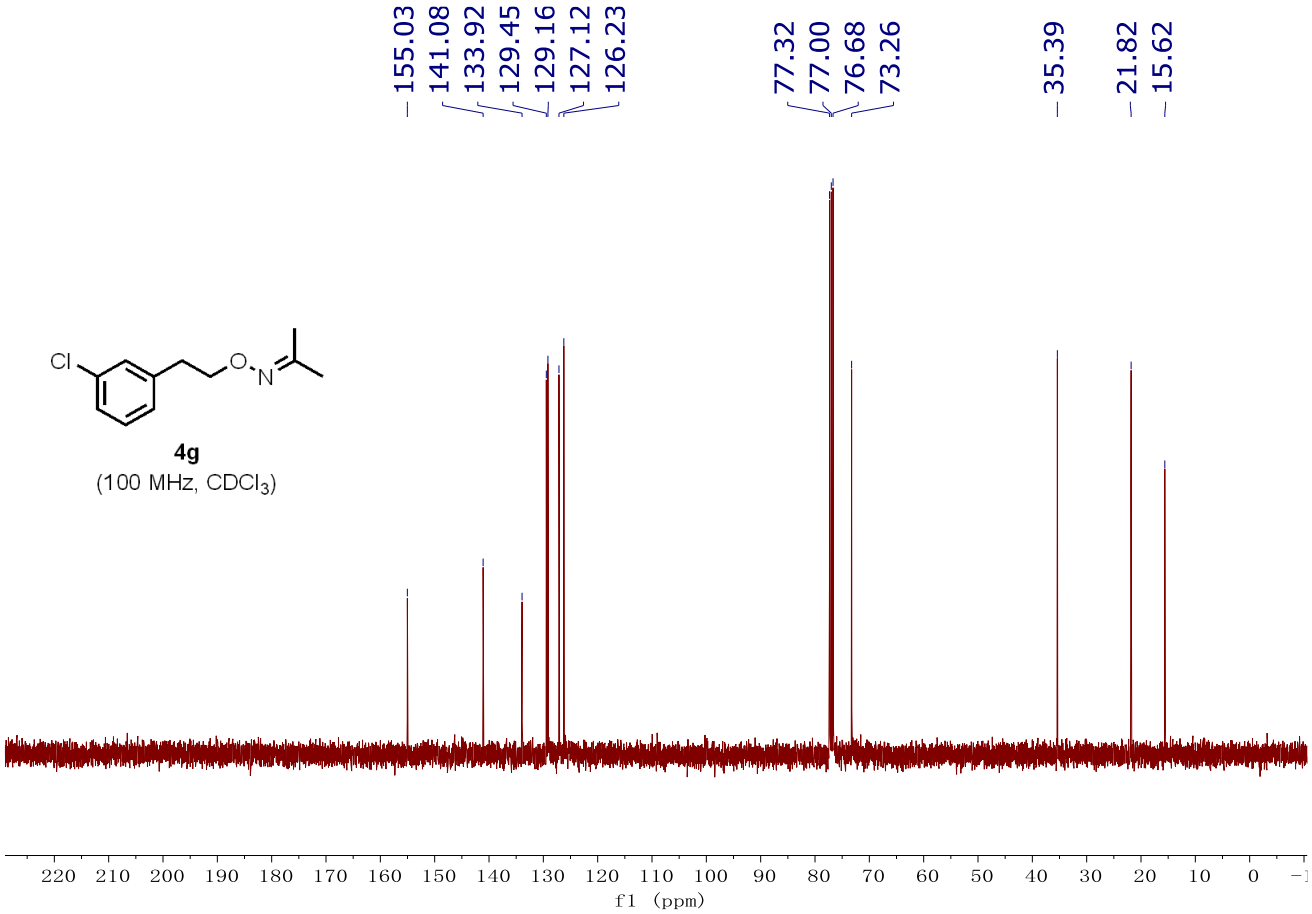
4f
(400 MHz, $CDCl_3$)

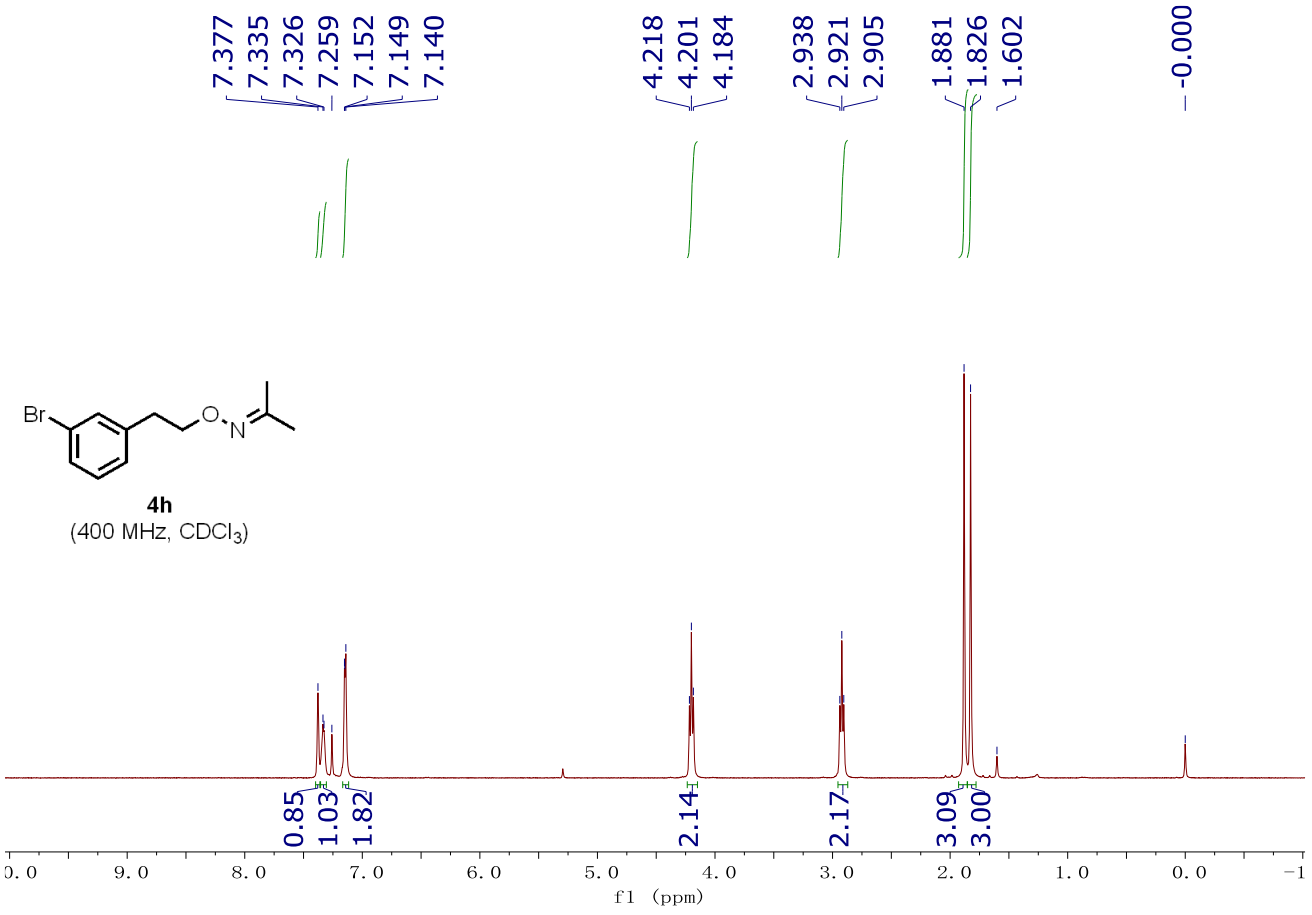


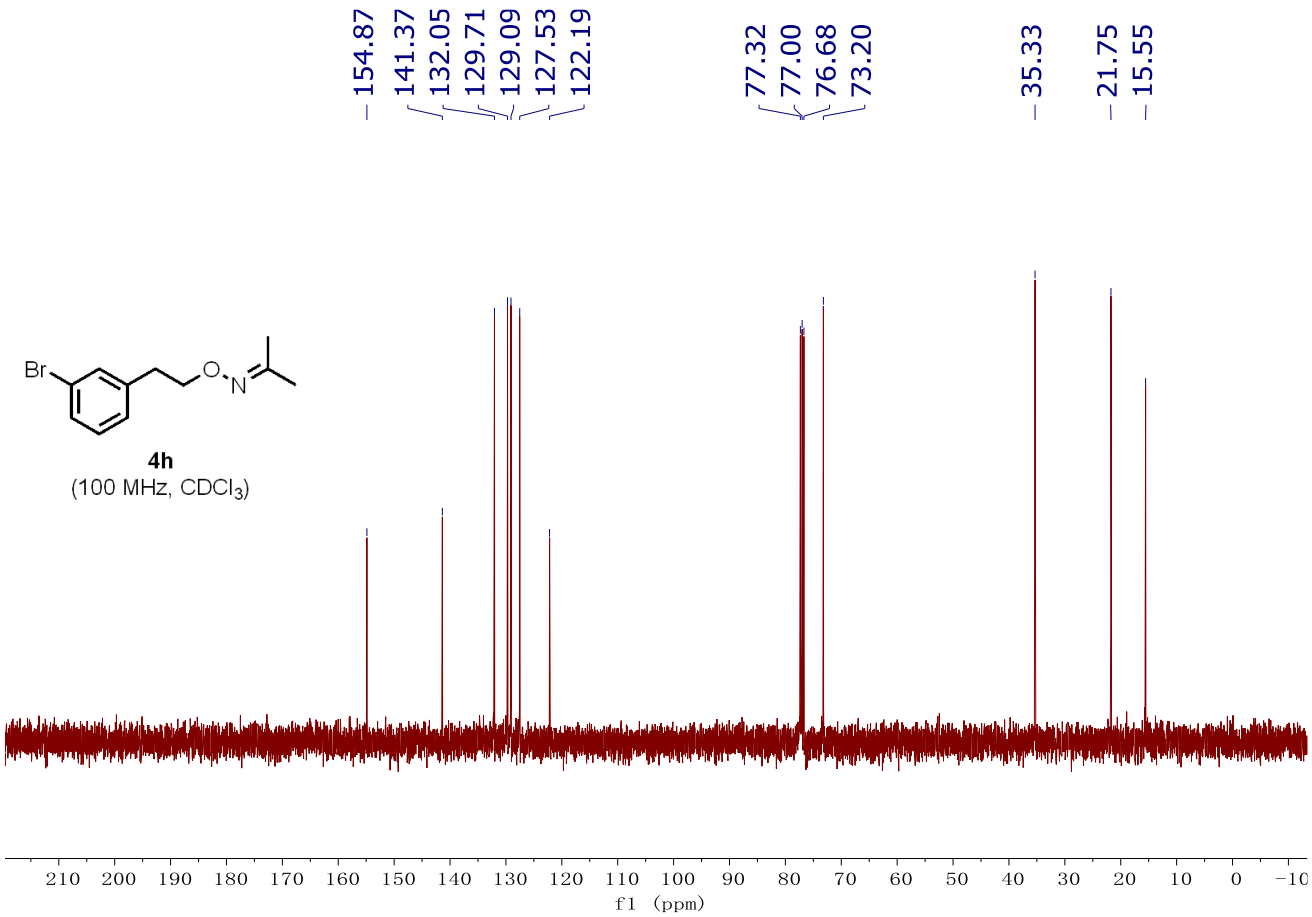
4f
(100 MHz, $CDCl_3$)

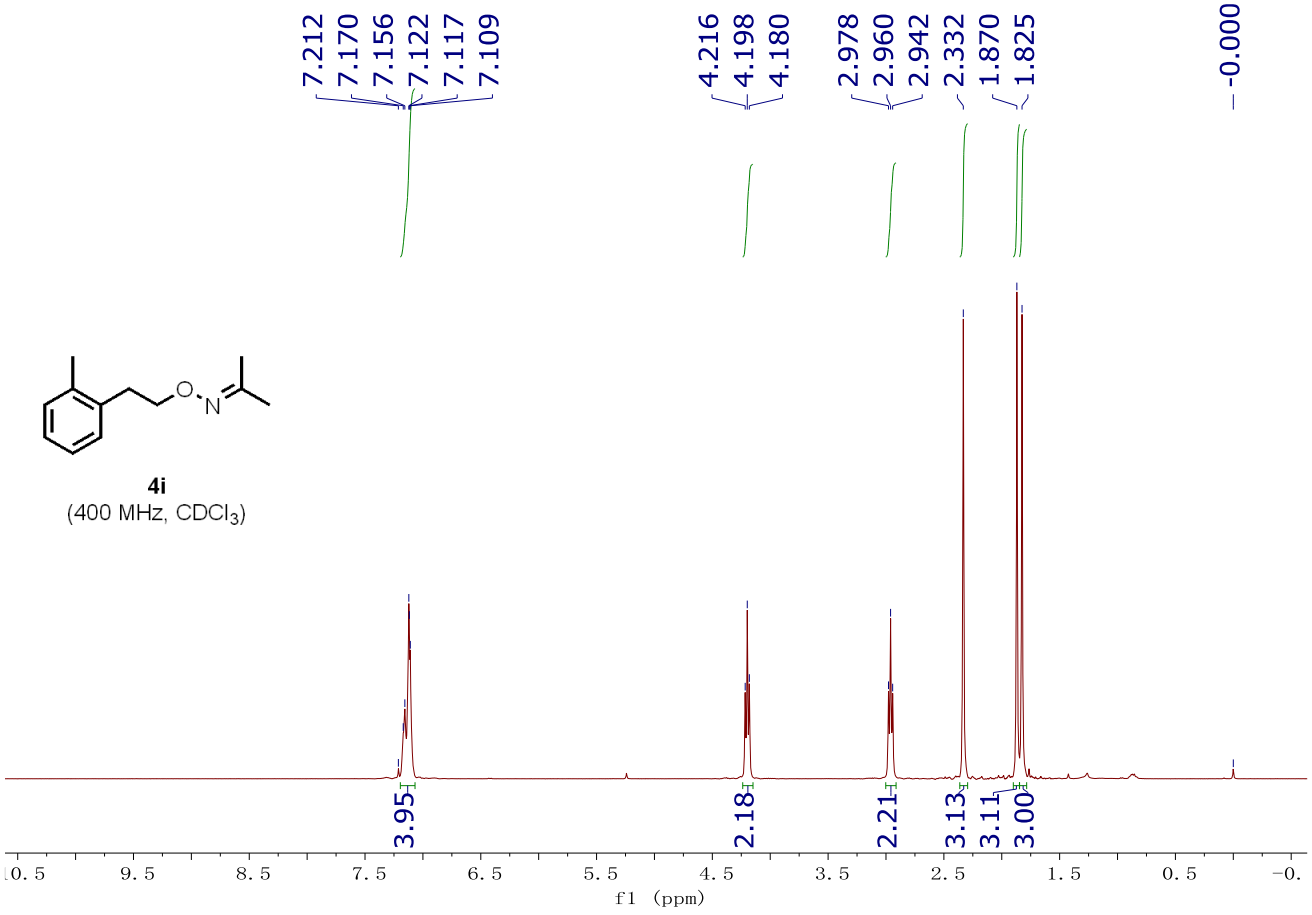

-0.000
-114.452
-114.468
-114.476
-114.491
-114.516
F
O
N
4f
(375 MHz, CDCl3)
f1 (ppm)

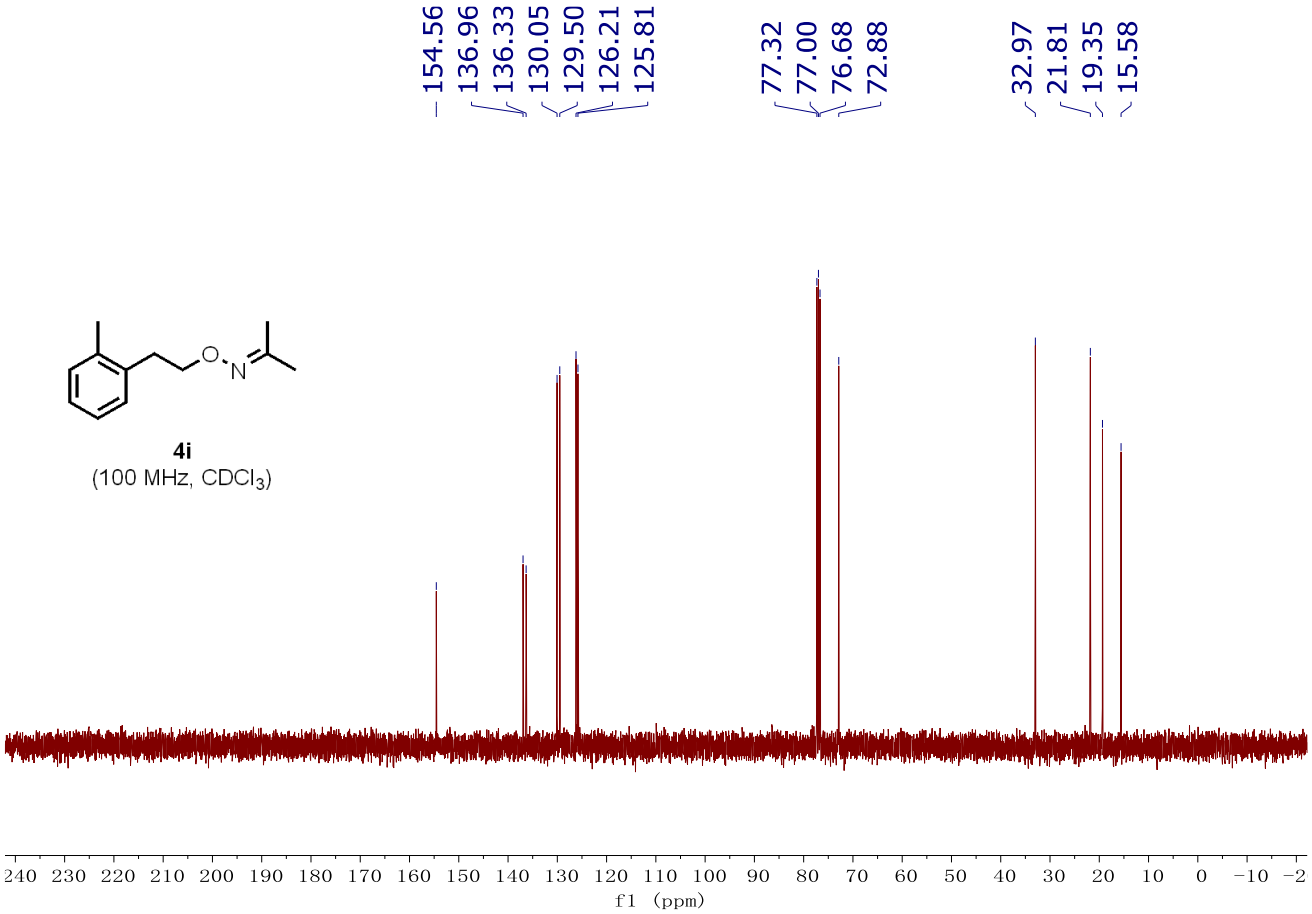

7.256
7.212
7.185
7.102
7.085
4.220
4.203
4.186
2.943
2.926
2.909
1.878
1.822
-0.000
Cl
O
N
4g
(400 MHz, CDCl3)
2.84
0.96
2.22
2.24
3.20
3.00
f1 (ppm)

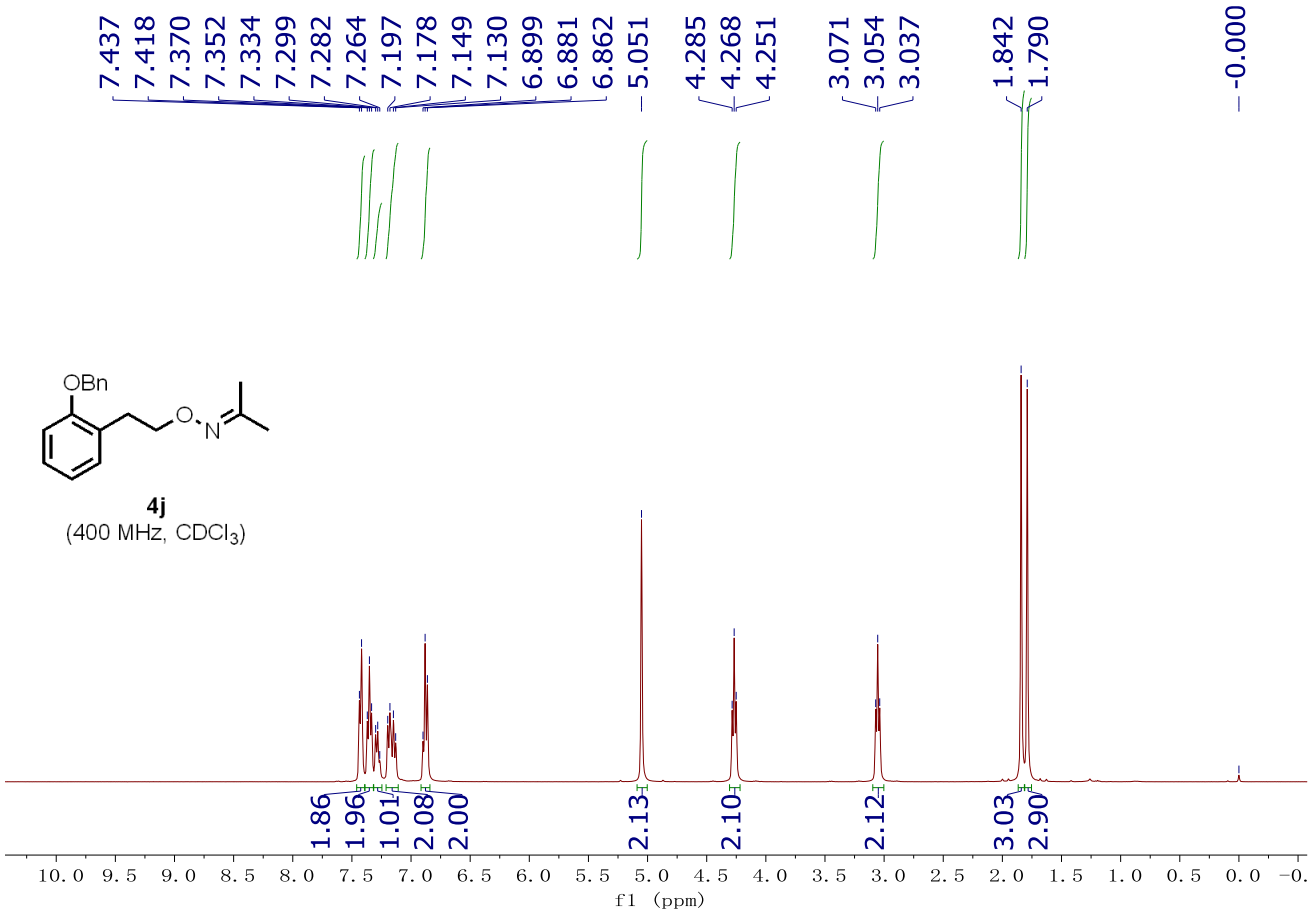

155.03
141.08
133.92
129.45
129.16
127.12
126.23
77.32
77.00
76.68
73.26
35.39
21.82
15.62
Cl
O
N
4g
(100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

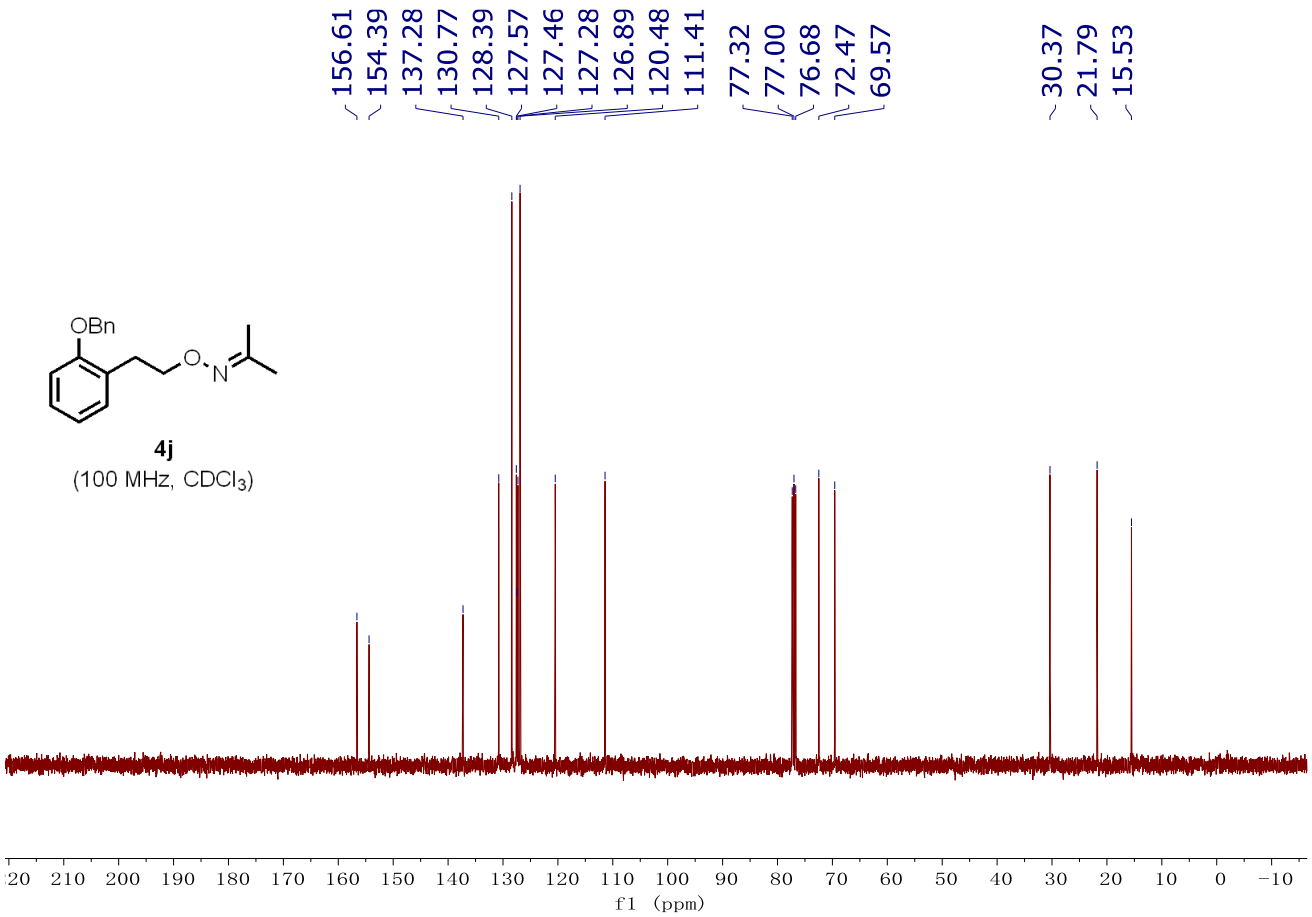

7.377
7.335
7.326
7.259
7.152
7.149
7.140
4.218
4.201
4.184
2.938
2.921
2.905
1.881
1.826
1.602
-0.000
Br
O
N
4h
(400 MHz, CDCl3)
0.85
1.03
1.82
2.14
2.17
3.09
3.00
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)

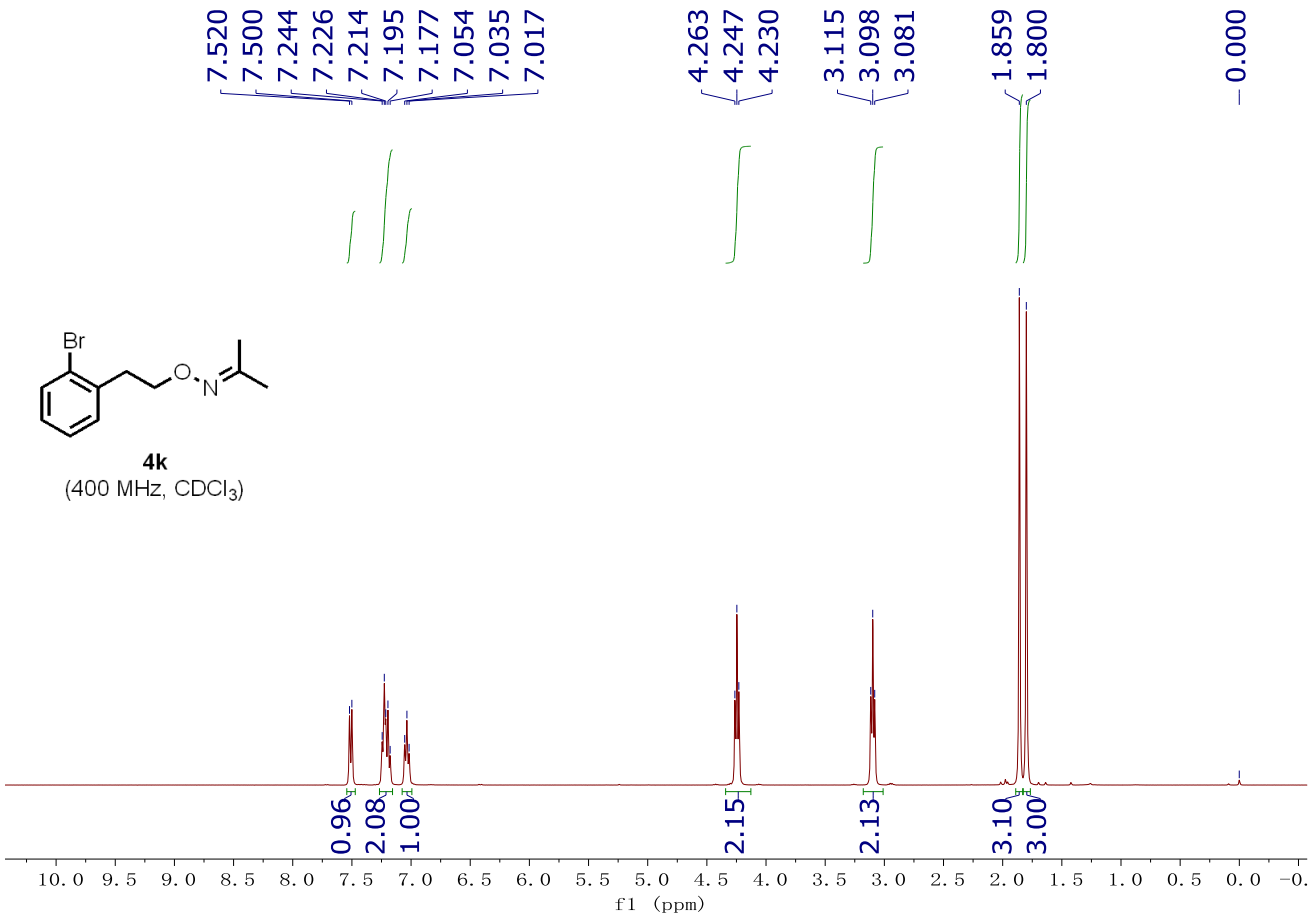

154.87
141.37
132.05
129.71
129.09
127.53
122.19
77.32
77.00
76.68
73.20
35.33
21.75
15.55
Br
O
N
4h
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

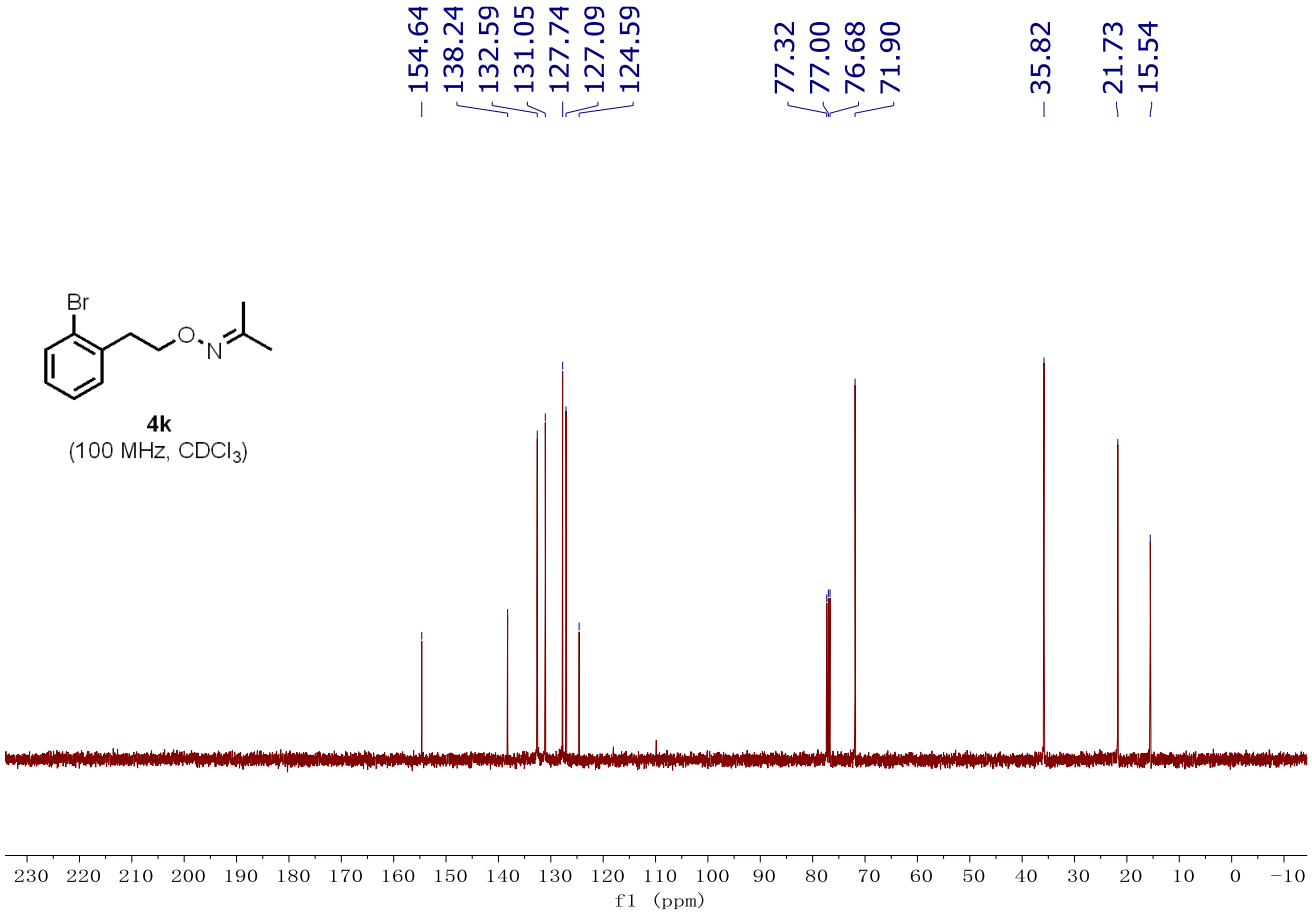

7.212
7.170
7.156
7.122
7.117
7.109
4.216
4.198
4.180
2.978
2.960
2.942
2.332
1.870
1.825
-0.000
O
N
4i
(400 MHz, CDCl3)
3.95
2.18
2.21
3.13
3.11
3.00
0.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)

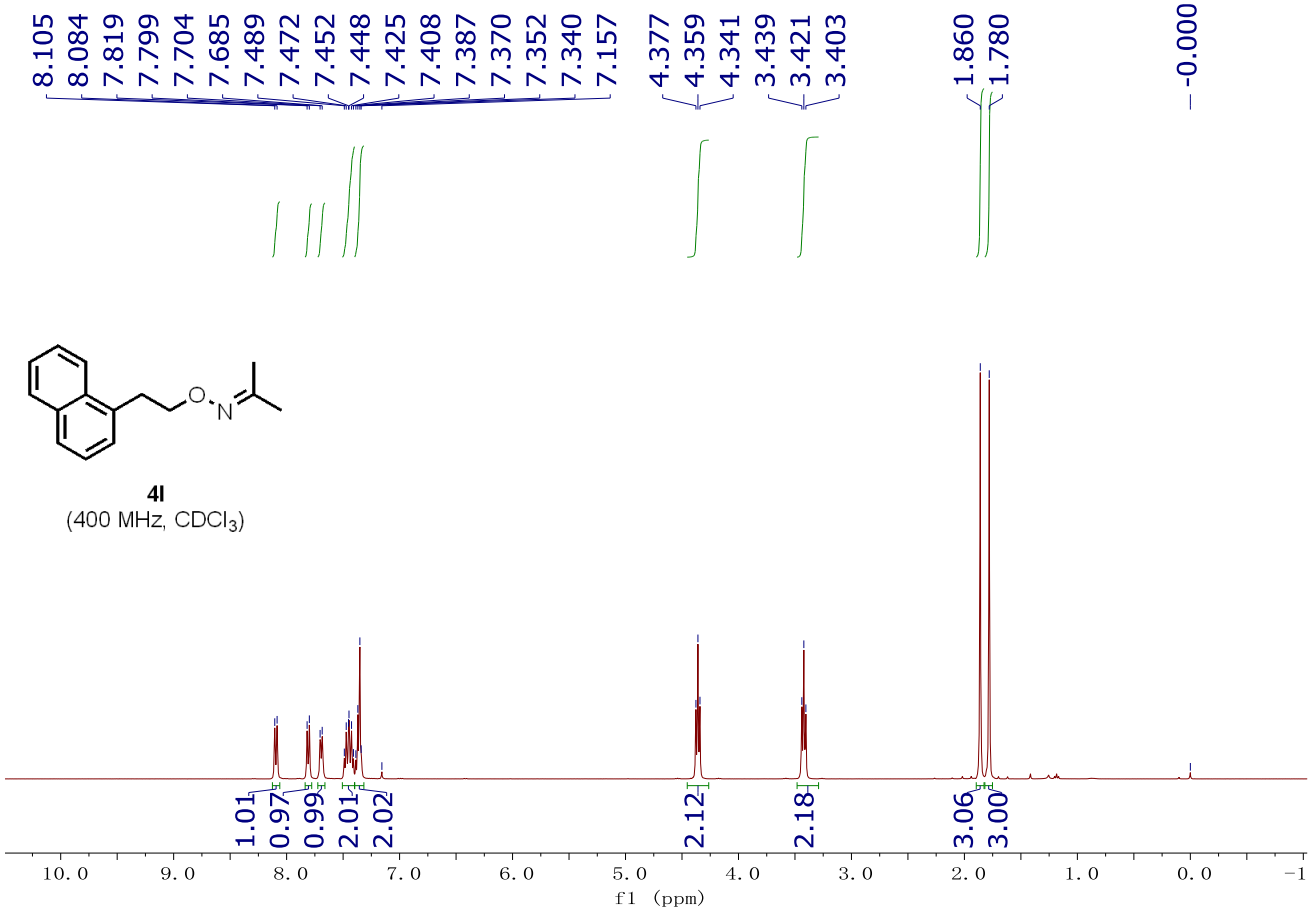

154.56
136.96
136.33
130.05
129.50
126.21
125.81
77.32
77.00
76.68
72.88
32.97
21.81
19.35
15.58
O
N
4i
(100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −2
f1 (ppm)

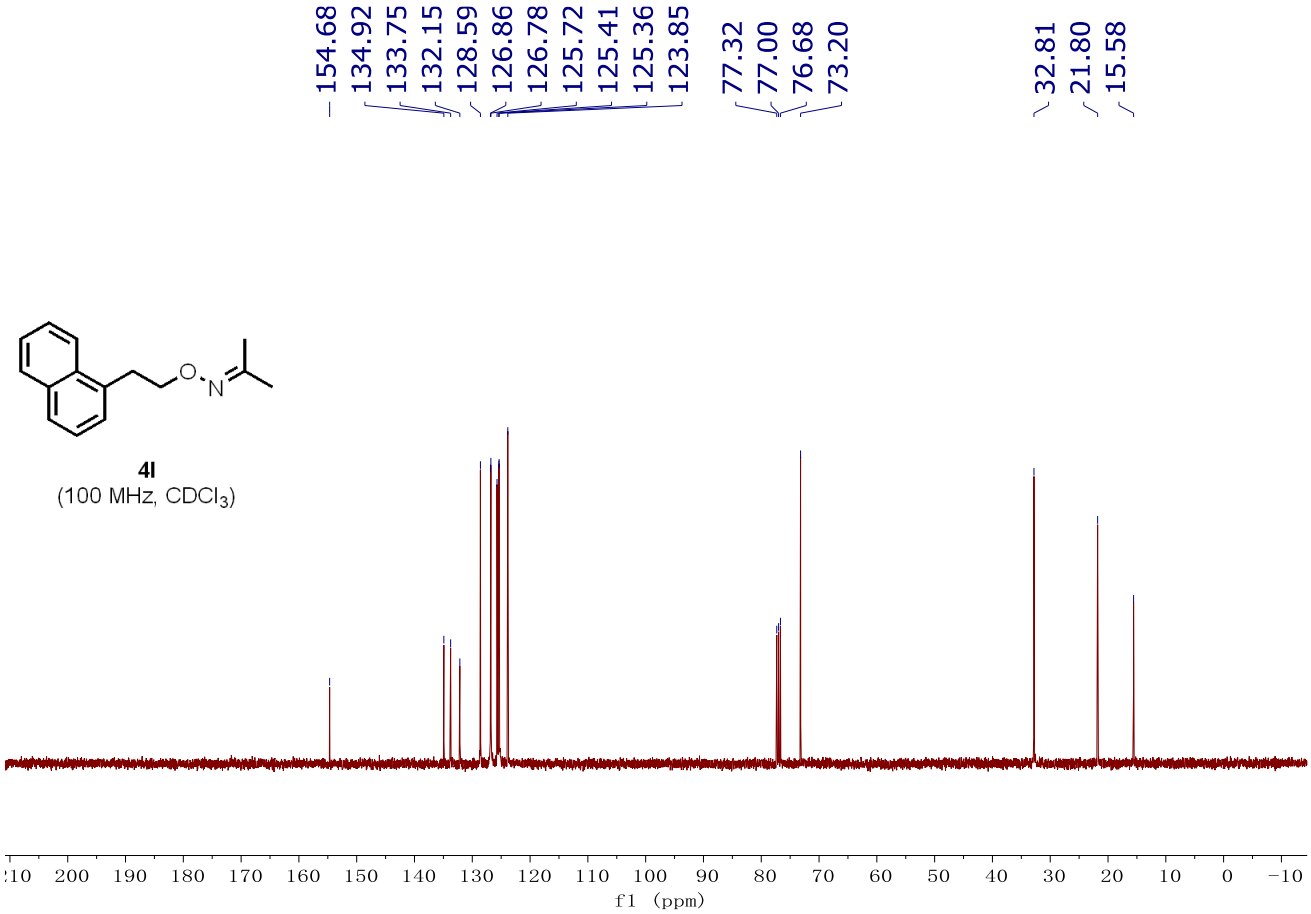

7.437
7.418
7.370
7.352
7.334
7.299
7.282
7.264
7.197
7.178
7.149
7.130
6.899
6.881
6.862
5.051
4.285
4.268
4.251
3.071
3.054
3.037
1.842
1.790
-0.000
OBn
O
N
4j
(400 MHz, CDCl3)
1.86
1.96
1.01
2.08
2.00
2.13
2.10
2.12
3.03
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

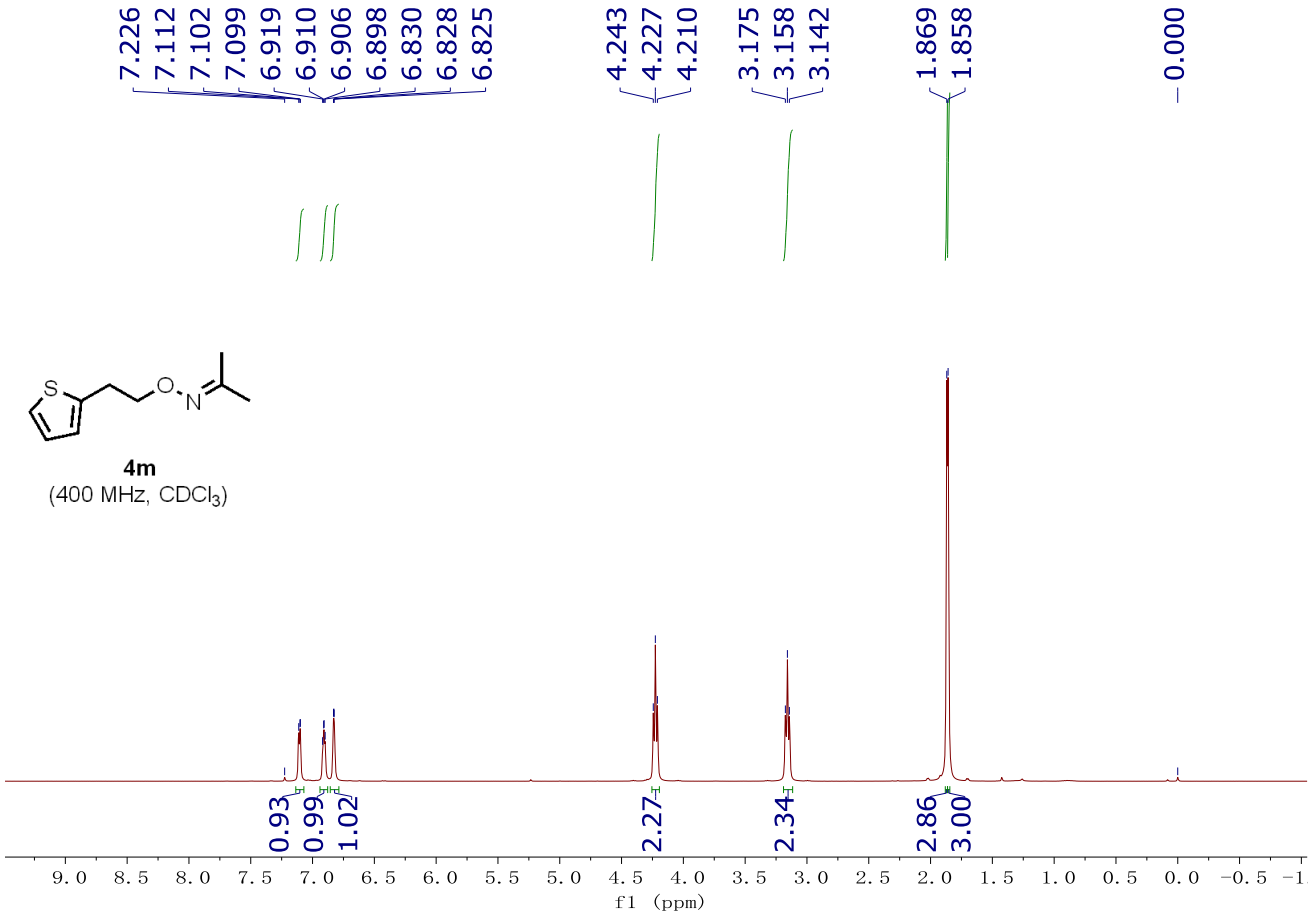

156.61
154.39
137.28
130.77
128.39
127.57
127.46
127.28
126.89
120.48
111.41
77.32
77.00
76.68
72.47
69.57
30.37
21.79
15.53
OBn
O
N
4j
(100 MHz, CDCl3)
f1 (ppm)

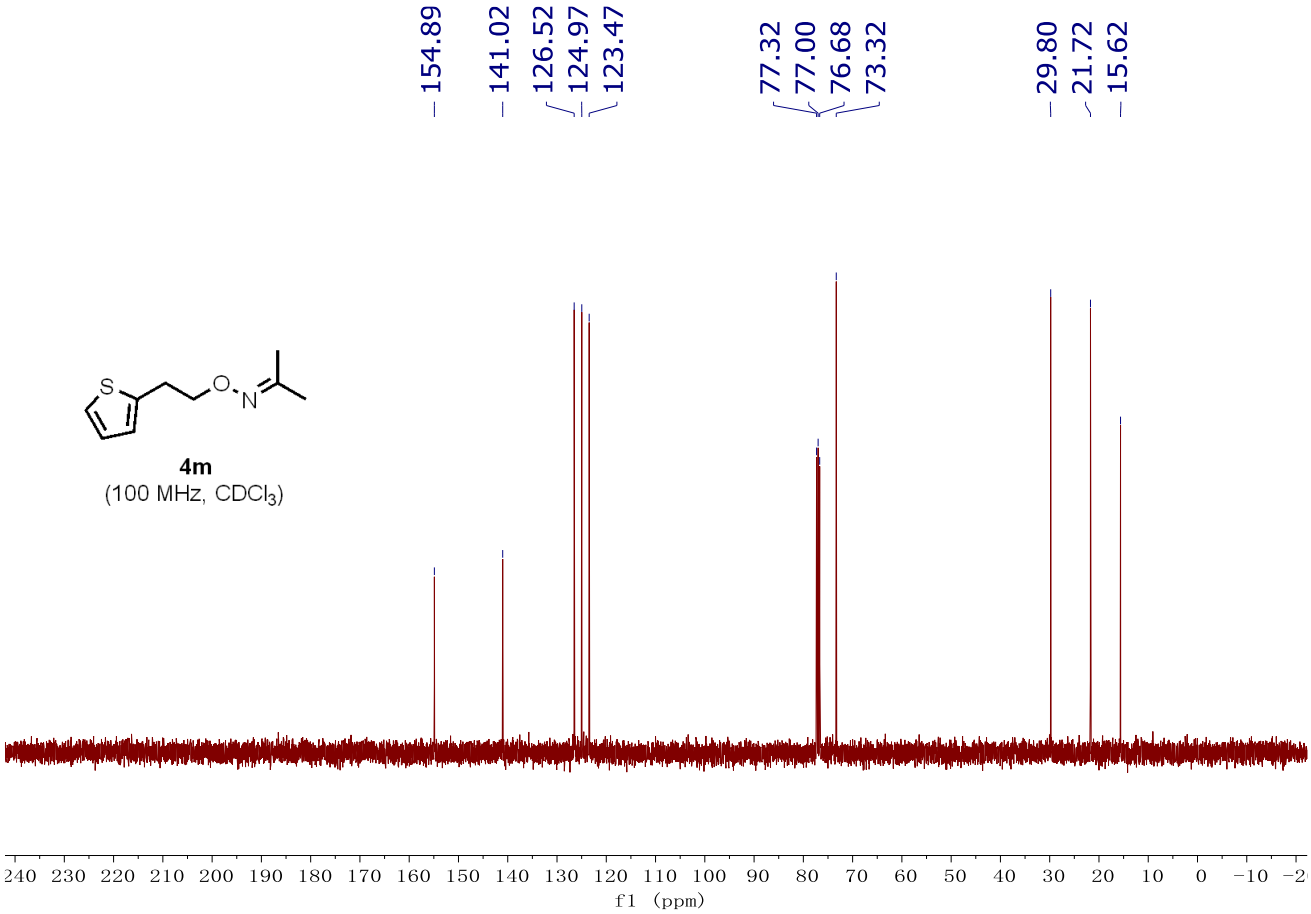

7.520
7.500
7.244
7.226
7.214
7.195
7.177
7.054
7.035
7.017
4.263
4.247
4.230
3.115
3.098
3.081
1.859
1.800
0.000
Br
O
N
4k
(400 MHz, CDCl3)
0.96
2.08
1.00
2.15
2.13
3.10
3.00
f1 (ppm)

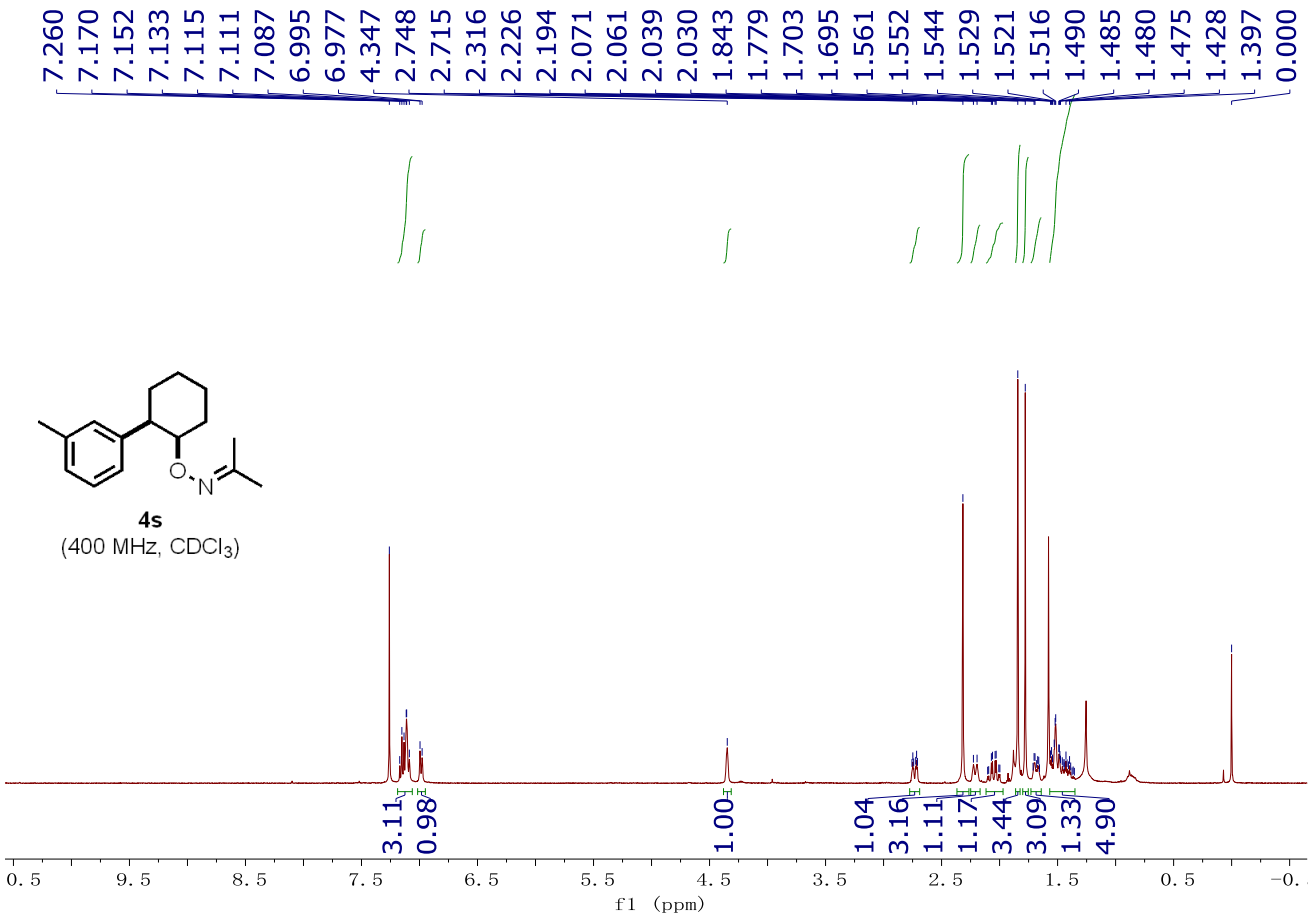

154.64
138.24
132.59
131.05
127.74
127.09
124.59
77.32
77.00
76.68
71.90
35.82
21.73
15.54
Br
O
N
4k
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

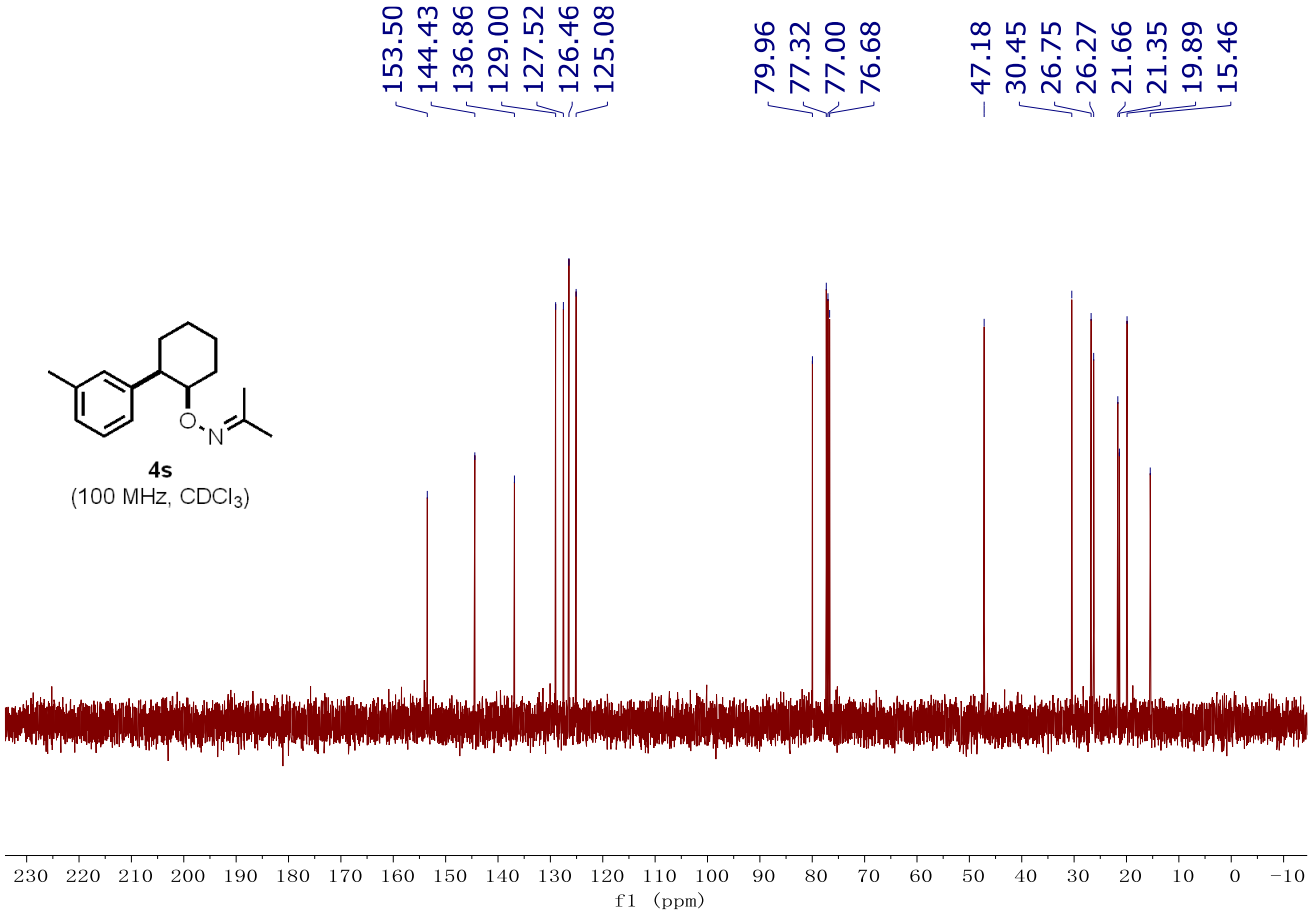

8.105
8.084
7.819
7.799
7.704
7.685
7.489
7.472
7.452
7.448
7.425
7.408
7.387
7.370
7.352
7.340
7.157
4.377
4.359
4.341
3.439
3.421
3.403
1.860
1.780
-0.000
O
N
4l
(400 MHz, CDCl3)
1.01
0.97
0.99
2.01
2.02
2.12
2.18
3.06
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1
f1 (ppm)

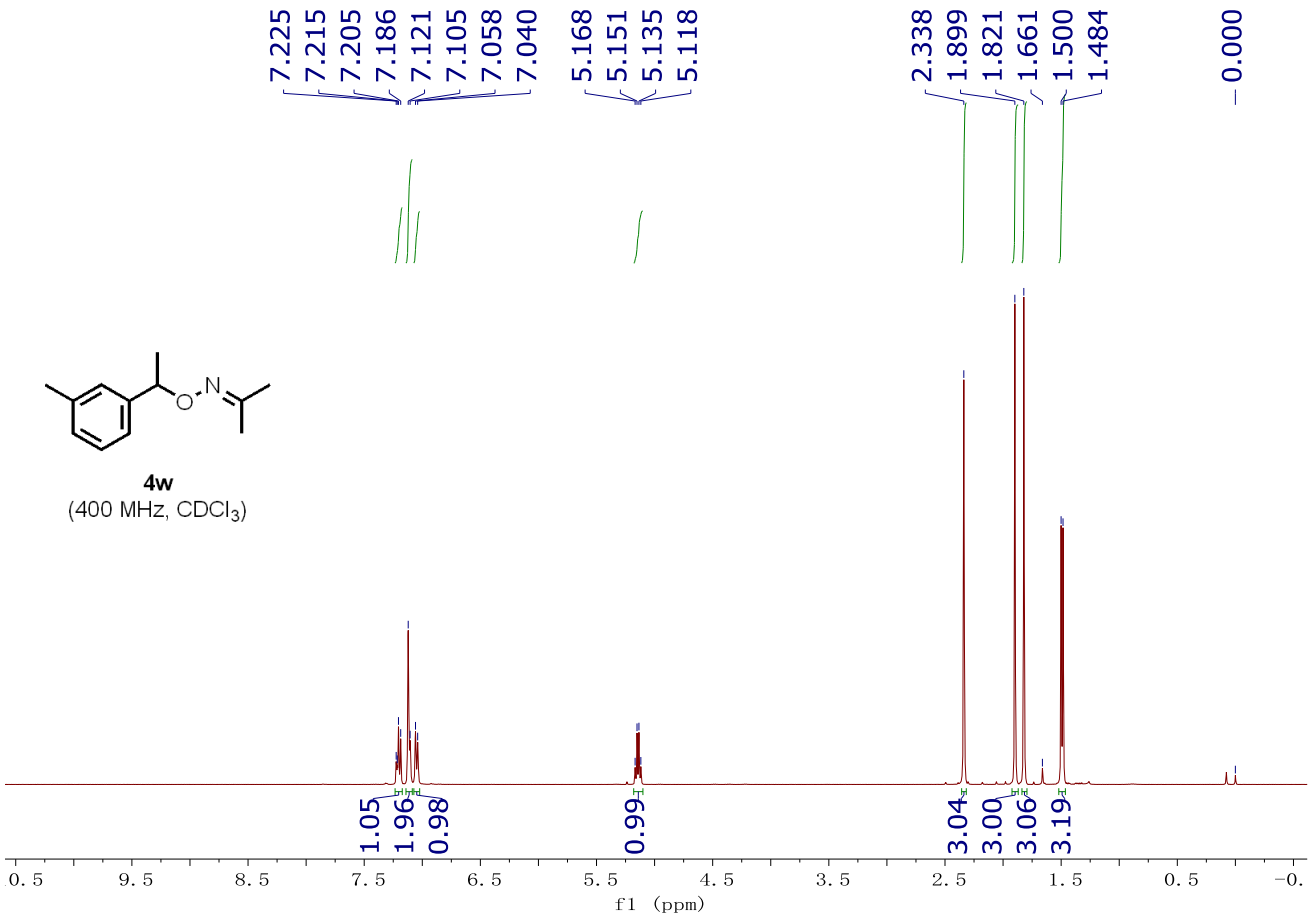

154.68
134.92
133.75
132.15
128.59
126.86
126.78
125.72
125.41
125.36
123.85
77.32
77.00
76.68
73.20
32.81
21.80
15.58
O
N
4l
(100 MHz, CDCl3)
f1 (ppm)

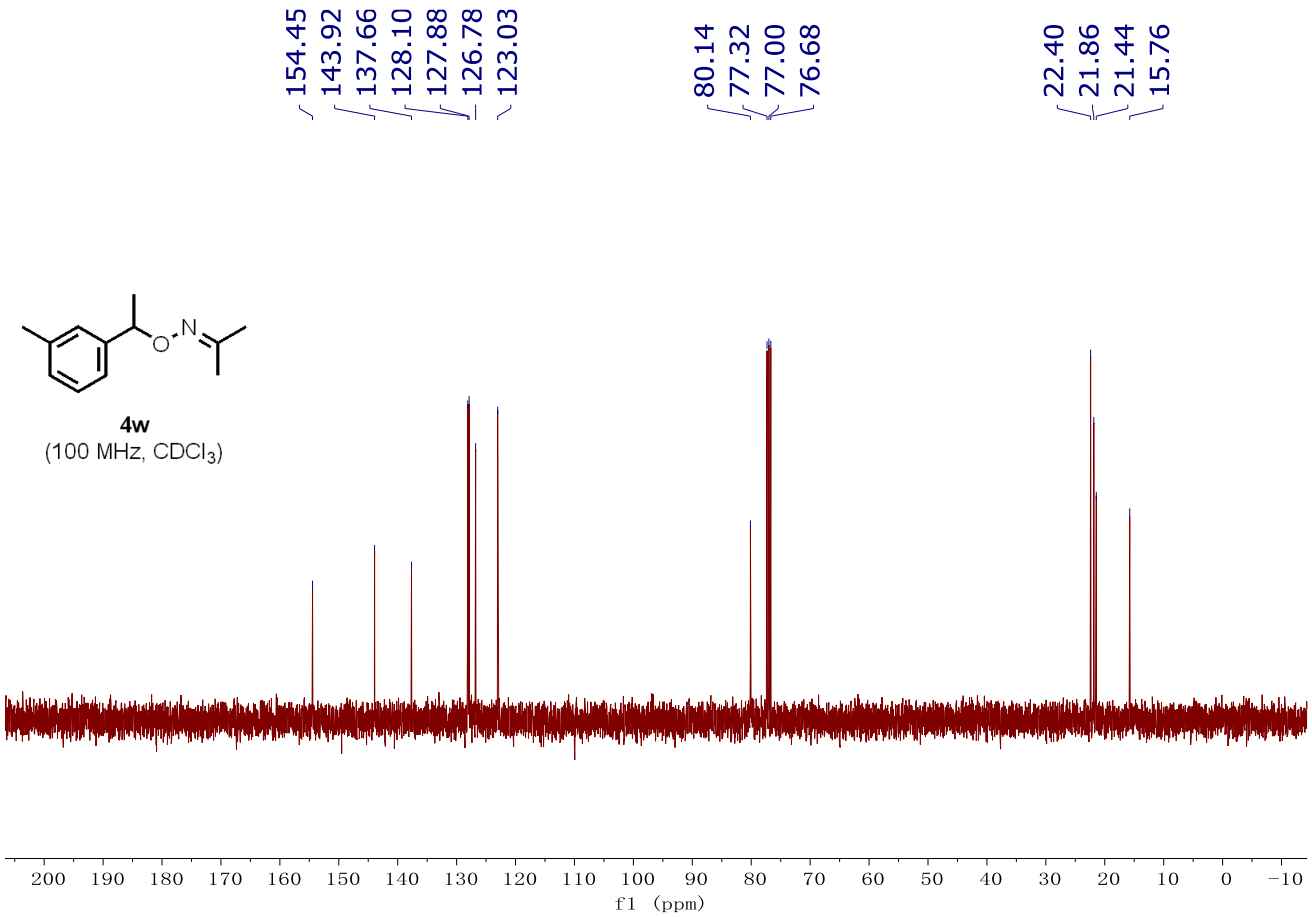

7.226
7.112
7.102
7.099
6.919
6.910
6.906
6.898
6.830
6.828
6.825
4.243
4.227
4.210
3.175
3.158
3.142
1.869
1.858
0.000
S
O
N
4m
(400 MHz, CDCl3)
0.93
0.99
1.02
2.27
2.34
2.86
3.00
f1 (ppm)

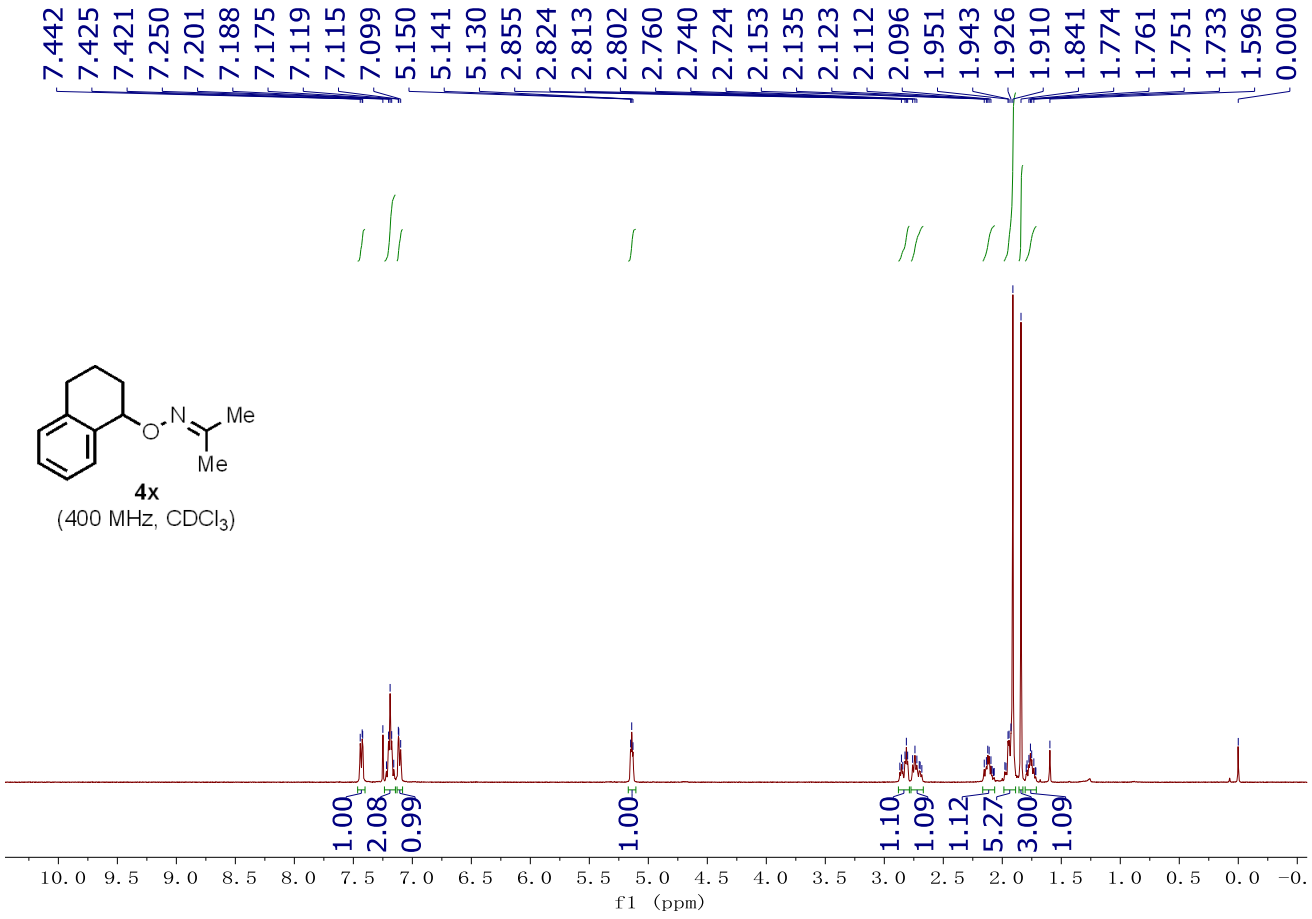

154.89
141.02
126.52
124.97
123.47
77.32
77.00
76.68
73.32
29.80
21.72
15.62
S
O
N
4m
(100 MHz, CDCl3)
f1 (ppm)

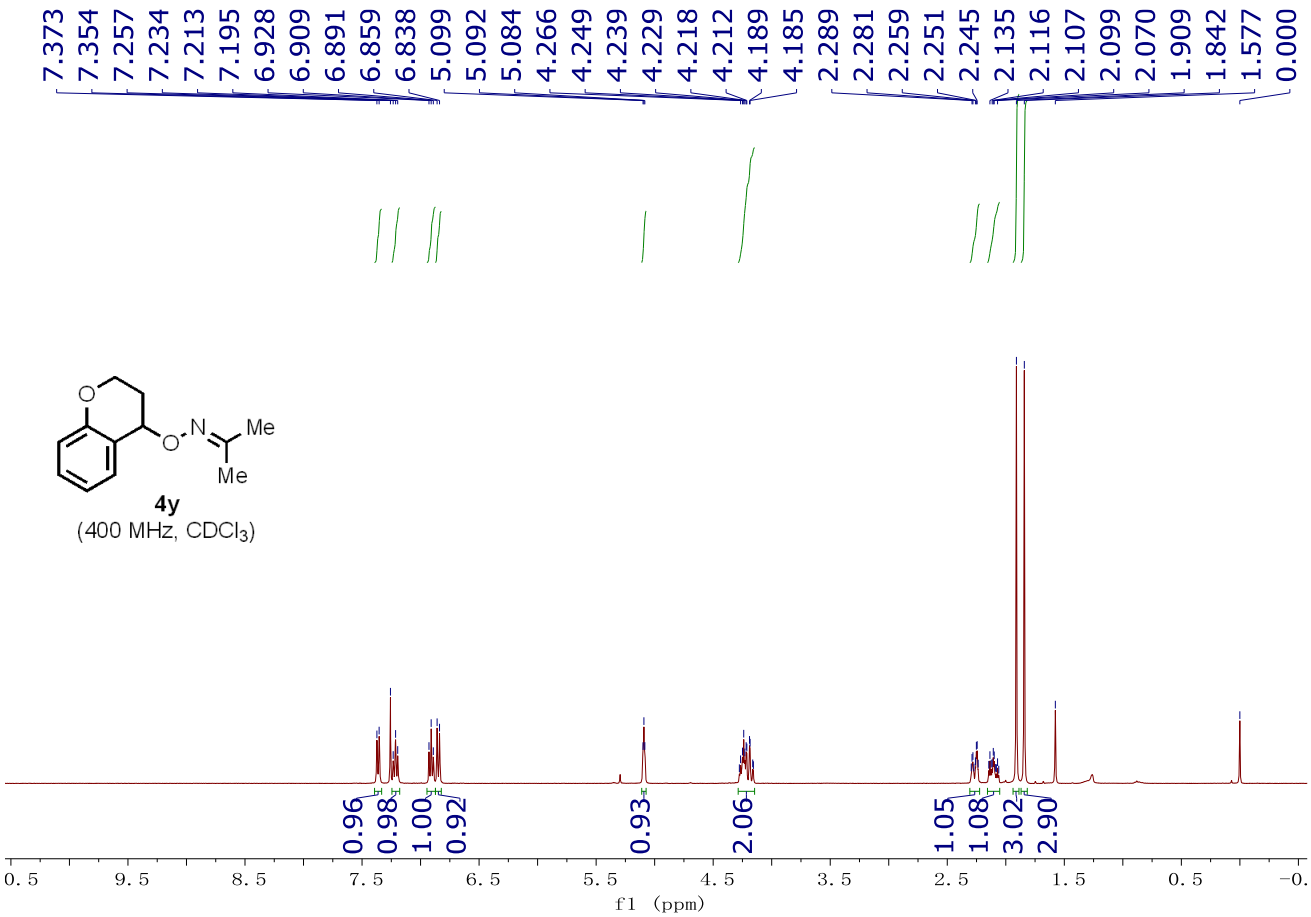

7.260
7.170
7.152
7.133
7.115
7.111
7.087
6.995
6.977
4.347
2.748
2.715
2.316
2.226
2.194
2.071
2.061
2.039
2.030
1.843
1.779
1.703
1.695
1.561
1.552
1.544
1.529
1.521
1.516
1.490
1.485
1.480
1.475
1.428
1.397
0.000
O
N
4s
(400 MHz, CDCl3)
3.11
0.98
1.00
1.04
3.16
1.11
1.17
3.44
3.09
1.33
4.90
f1 (ppm)

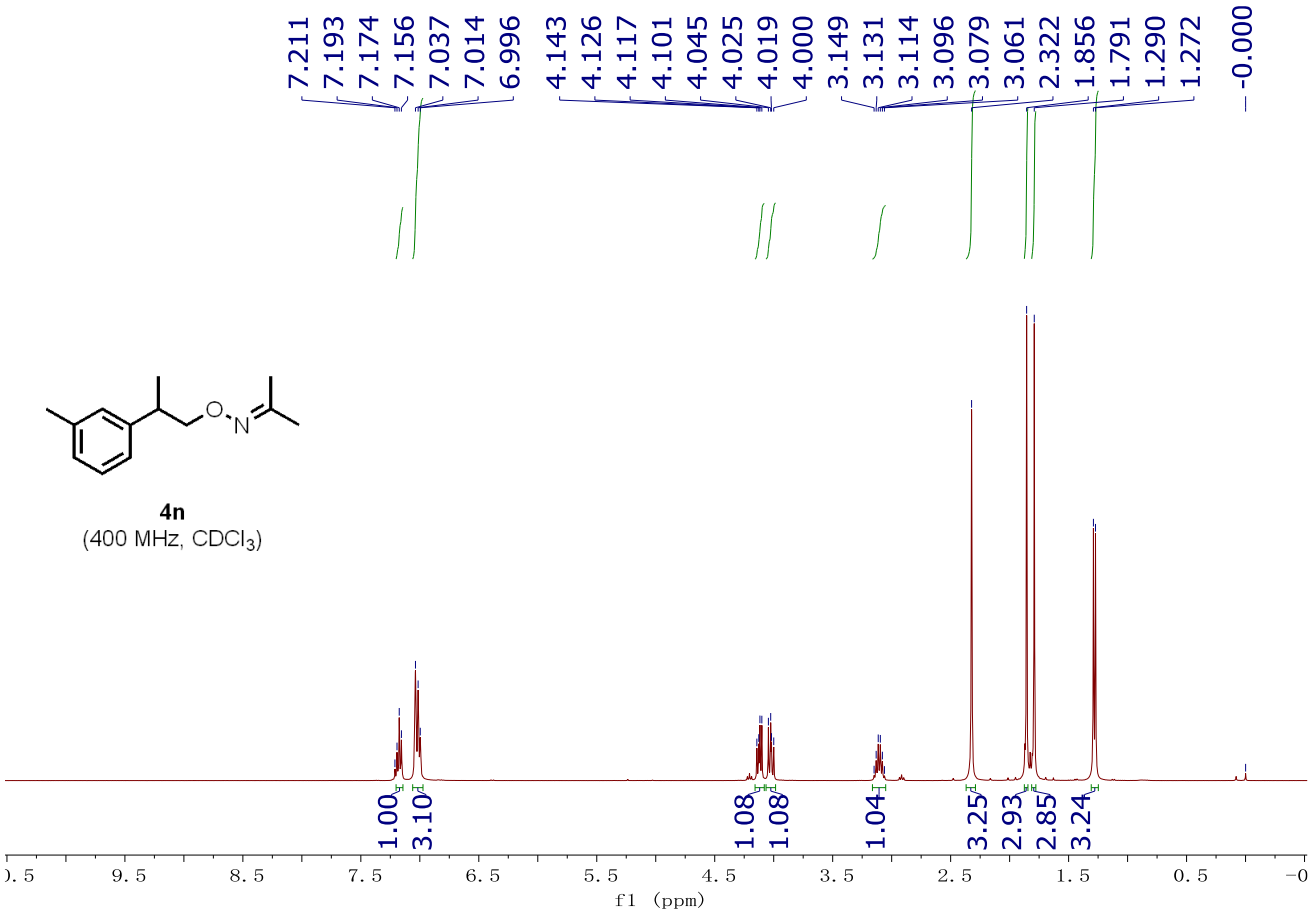

153.50
144.43
136.86
129.00
127.52
126.46
125.08
79.96
77.32
77.00
76.68
47.18
30.45
26.75
26.27
21.66
21.35
19.89
15.46
4s
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

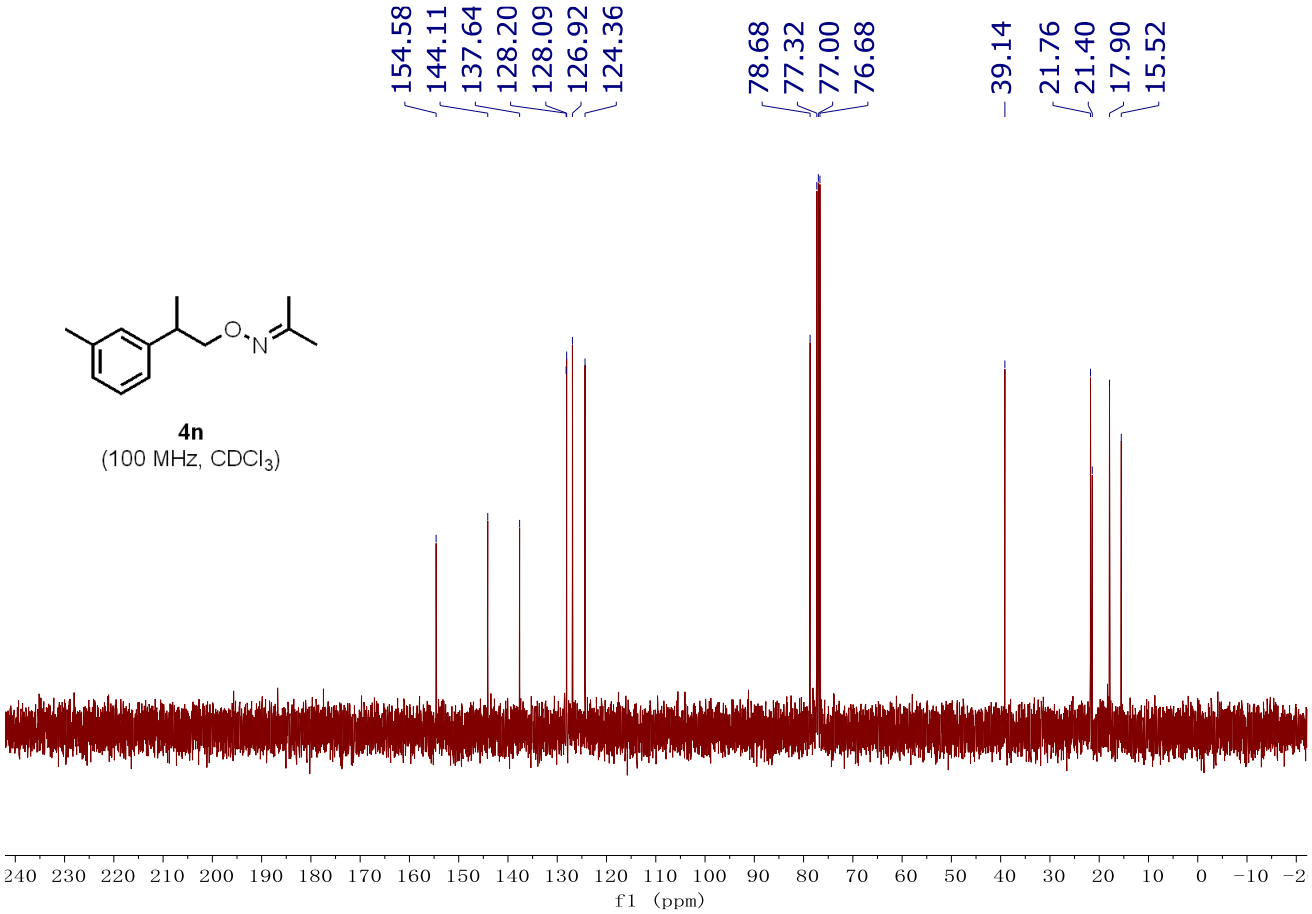

7.225
7.215
7.205
7.186
7.121
7.105
7.058
7.040
5.168
5.151
5.135
5.118
2.338
1.899
1.821
1.661
1.500
1.484
0.000
4w
(400 MHz, CDCl3)
1.05
1.96
0.98
0.99
3.04
3.00
3.06
3.19
0.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.
f1 (ppm)

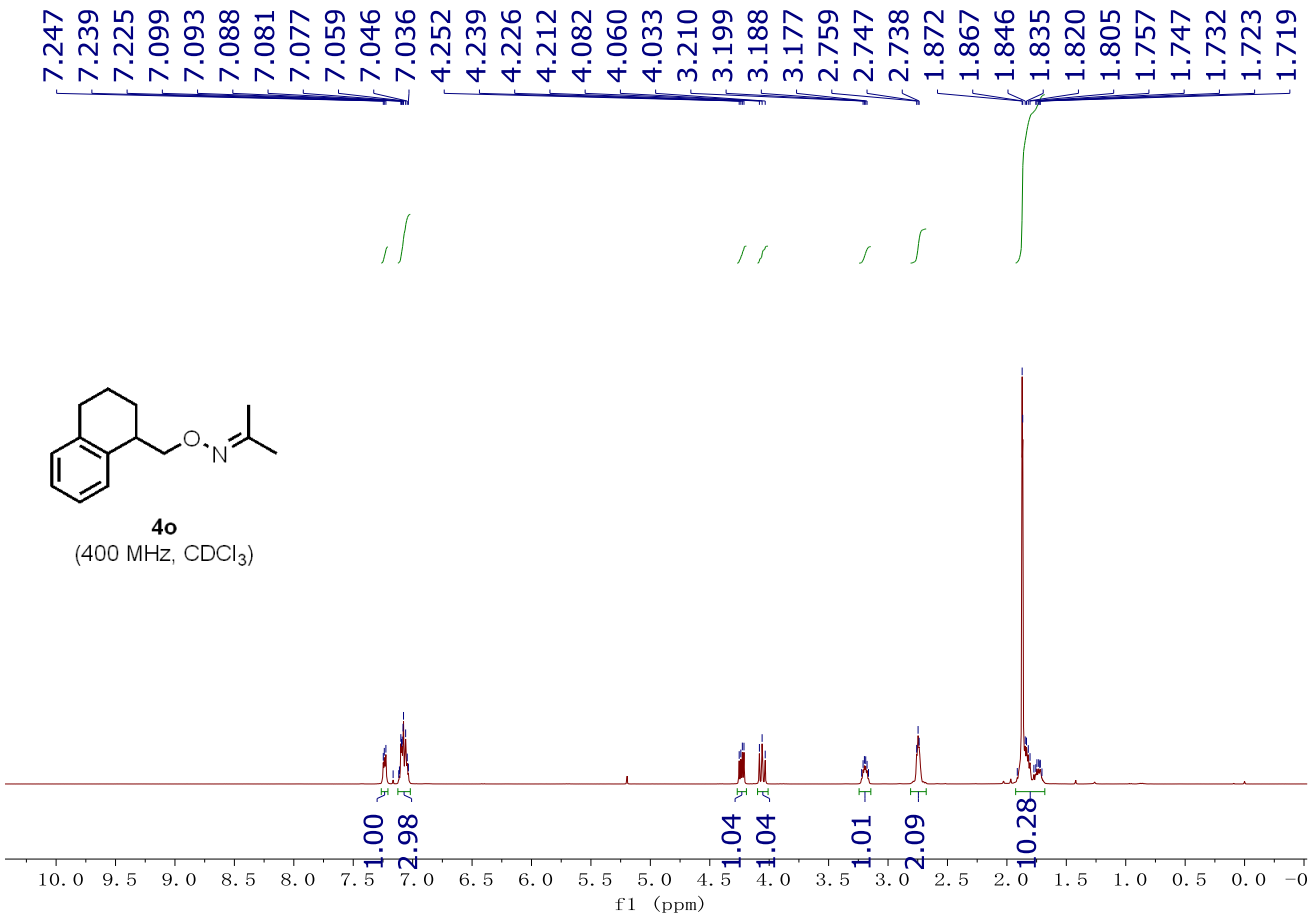

154.45
143.92
137.66
128.10
127.88
126.78
123.03
80.14
77.32
77.00
76.68
22.40
21.86
21.44
15.76
4w
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

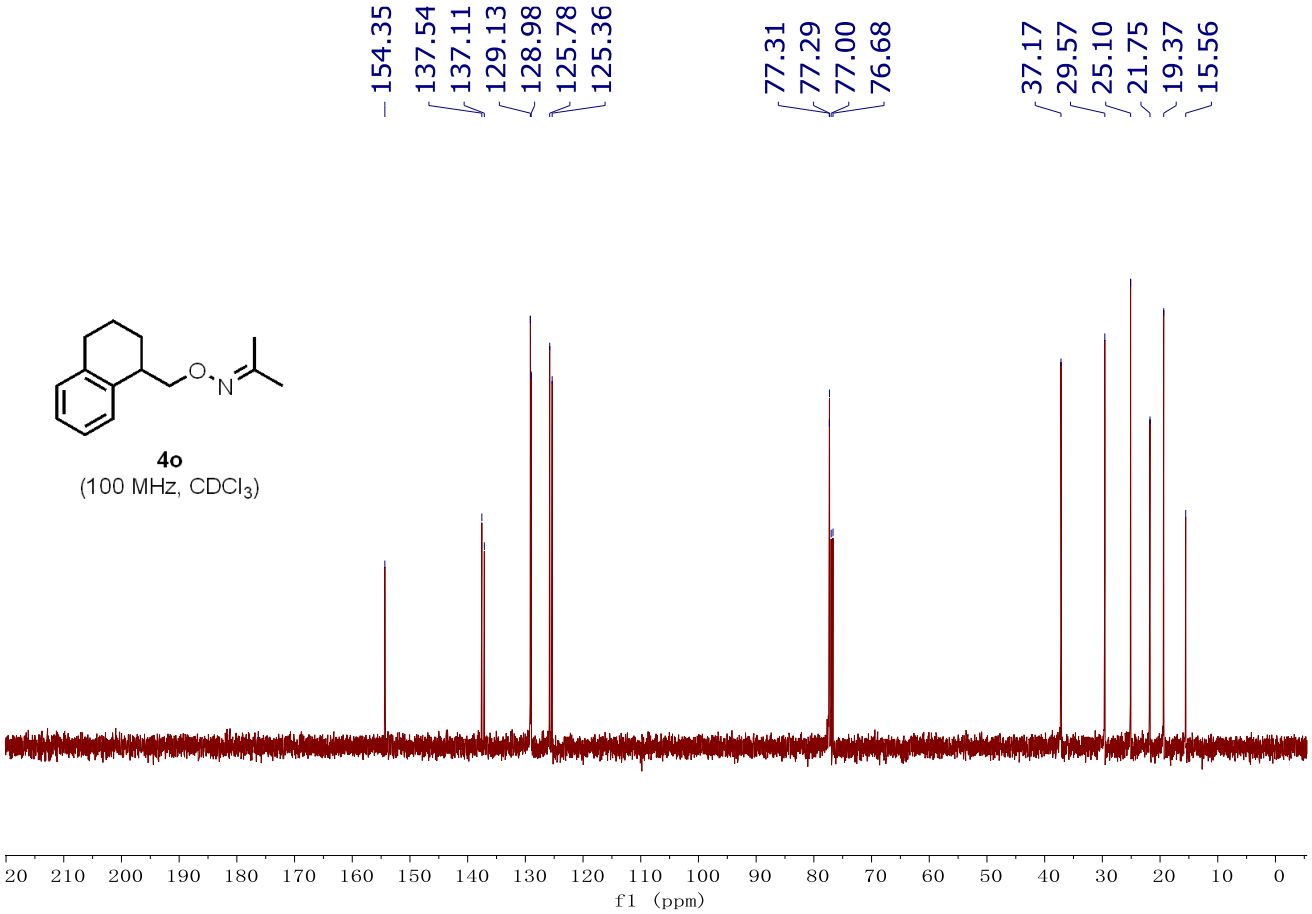

7.442
7.425
7.421
7.250
7.201
7.188
7.175
7.119
7.115
7.099
5.150
5.141
5.130
2.855
2.824
2.813
2.802
2.760
2.740
2.724
2.153
2.135
2.123
2.112
2.096
1.951
1.943
1.926
1.910
1.841
1.774
1.761
1.751
1.733
1.596
0.000
Me
Me
4x
(400 MHz, CDCl3)
1.00
2.08
0.99
1.00
1.10
1.09
1.12
5.27
3.00
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

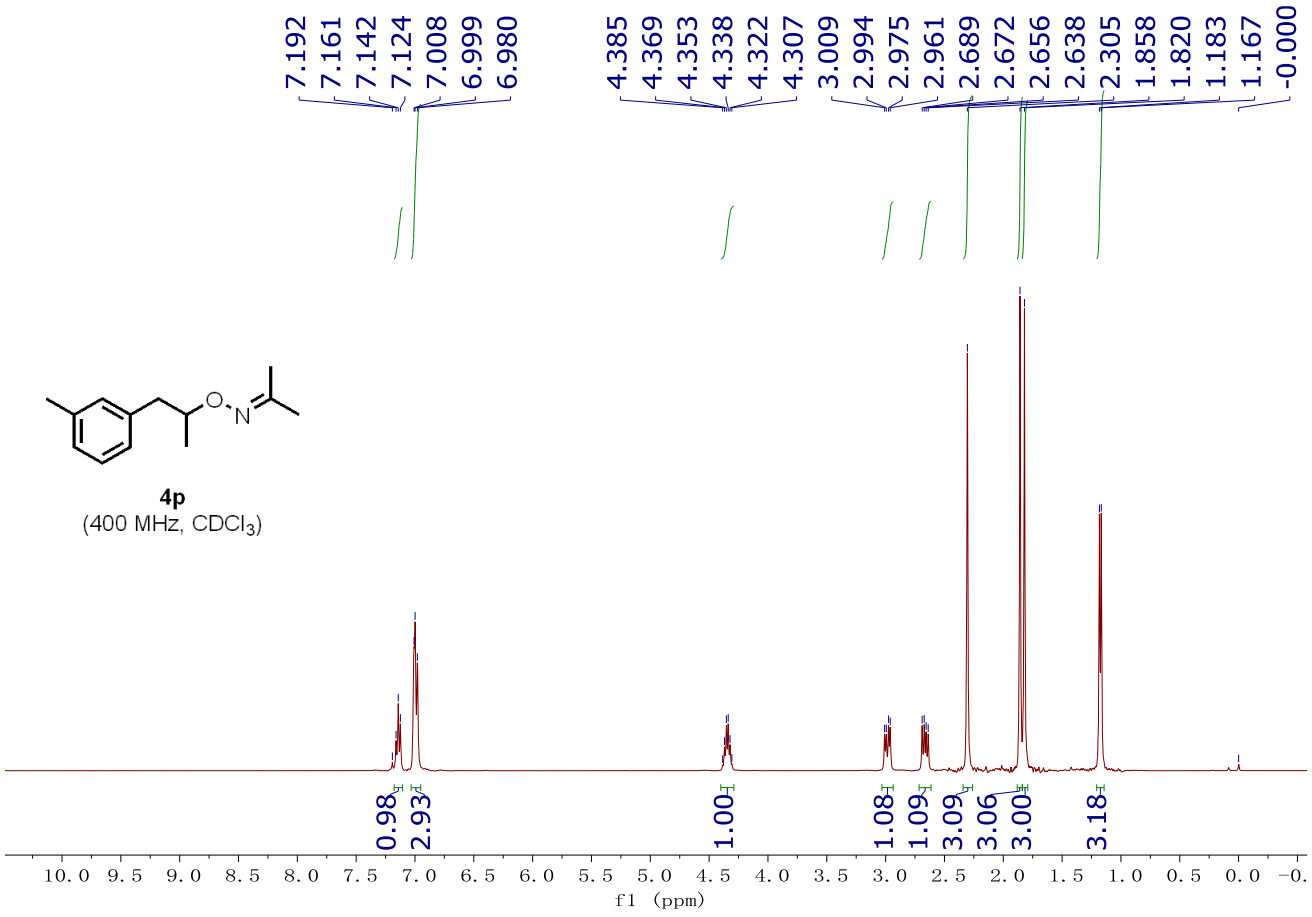

7.373
7.354
7.257
7.234
7.213
7.195
6.928
6.909
6.891
6.859
6.838
5.099
5.092
5.084
4.266
4.249
4.239
4.229
4.218
4.212
4.189
4.185
2.289
2.281
2.259
2.251
2.245
2.135
2.116
2.107
2.099
2.070
1.909
1.842
1.577
0.000
O
N
O
Me
Me
4y
(400 MHz, CDCl3)
0.96
0.98
1.00
0.92
0.93
2.06
1.05
1.08
3.02
2.90
f1 (ppm)

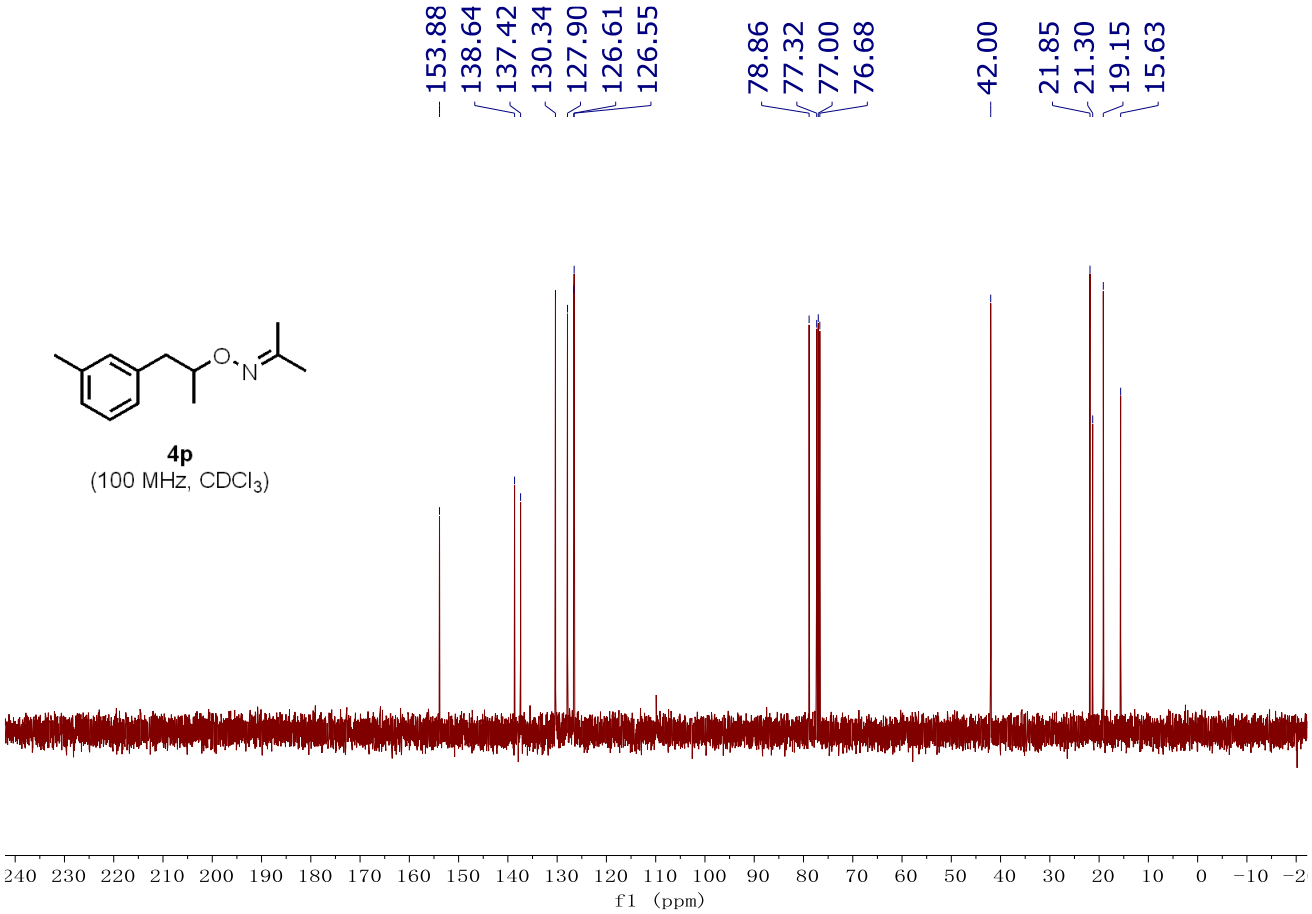

7.211
7.193
7.174
7.156
7.037
7.014
6.996
4.143
4.126
4.117
4.101
4.045
4.025
4.019
4.000
3.149
3.131
3.114
3.096
3.079
3.061
2.322
1.856
1.791
1.290
1.272
-0.000
O
N
4n
(400 MHz, CDCl3)
1.00
3.10
1.08
1.08
1.04
3.25
2.93
2.85
3.24
f1 (ppm)

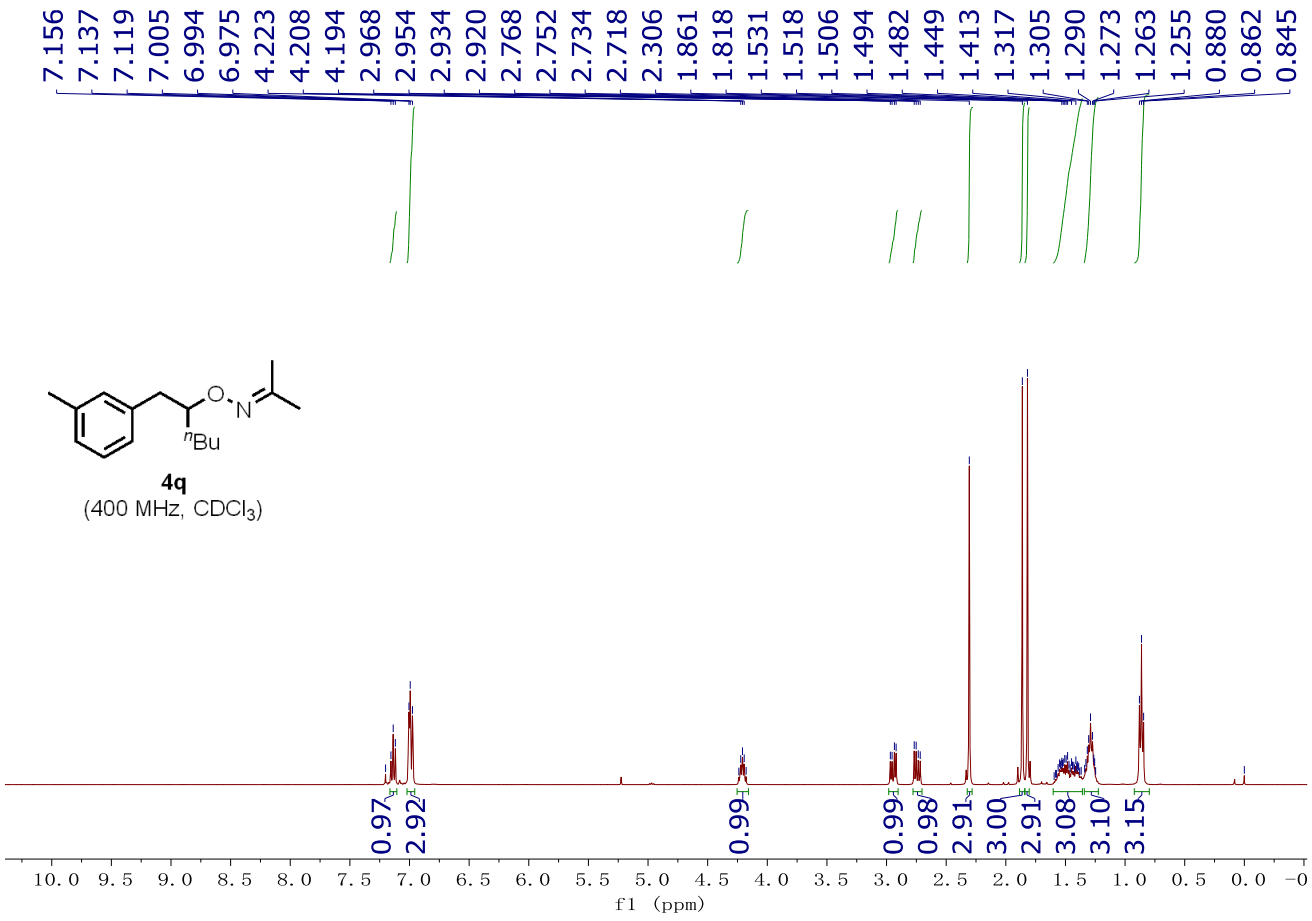

154.58
144.11
137.64
128.20
128.09
126.92
124.36
78.68
77.32
77.00
76.68
39.14
21.76
21.40
17.90
15.52
4n
(100 MHz, CDCl3)
f1 (ppm)

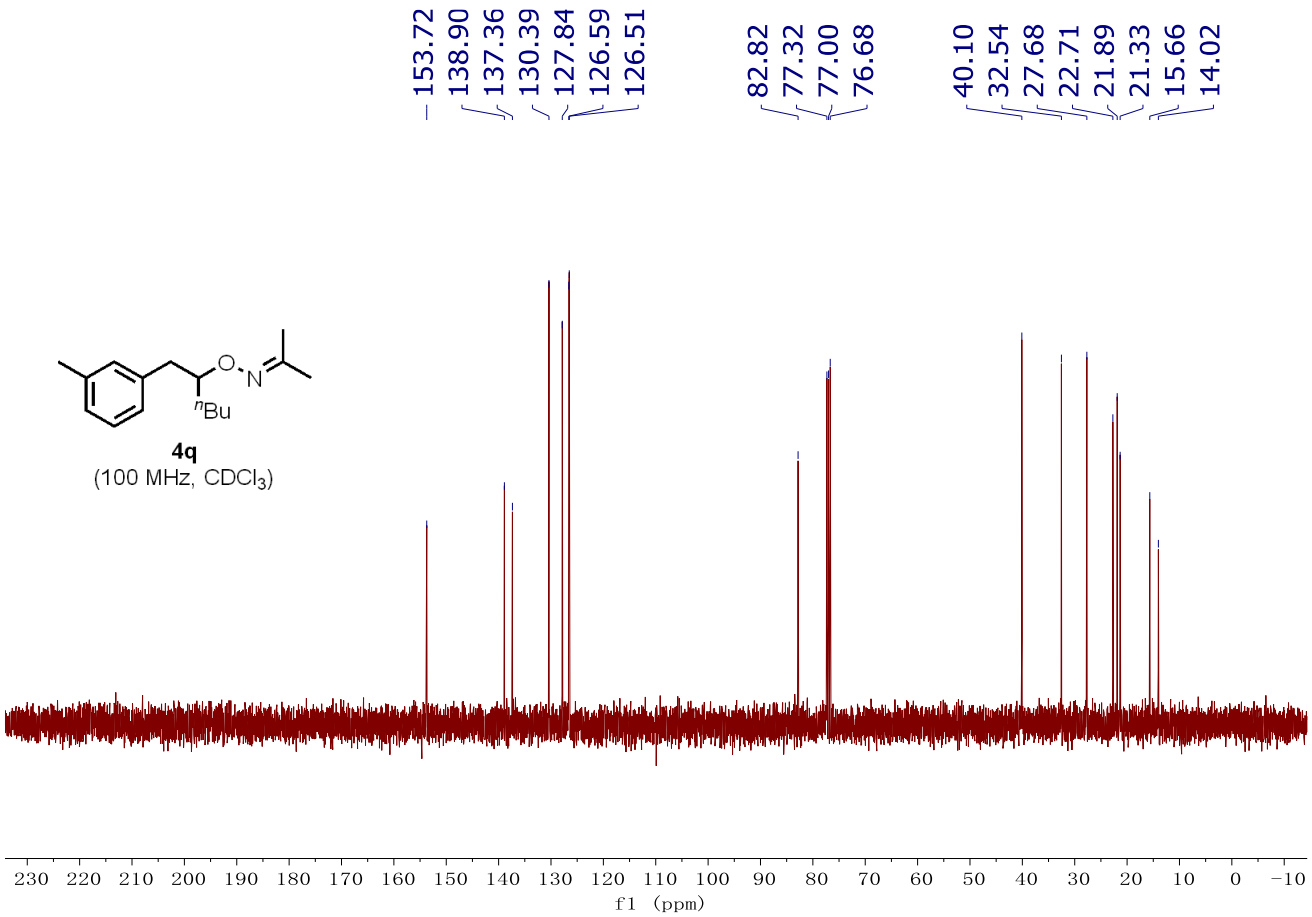

7.247
7.239
7.225
7.099
7.093
7.088
7.081
7.077
7.059
7.046
7.036
4.252
4.239
4.226
4.212
4.082
4.060
4.033
3.210
3.199
3.188
3.177
2.759
2.747
2.738
1.872
1.867
1.846
1.835
1.820
1.805
1.757
1.747
1.732
1.723
1.719
1.00
2.98
1.04
1.04
1.01
2.09
10.28
4o
(400 MHz, CDCl3)
f1 (ppm)

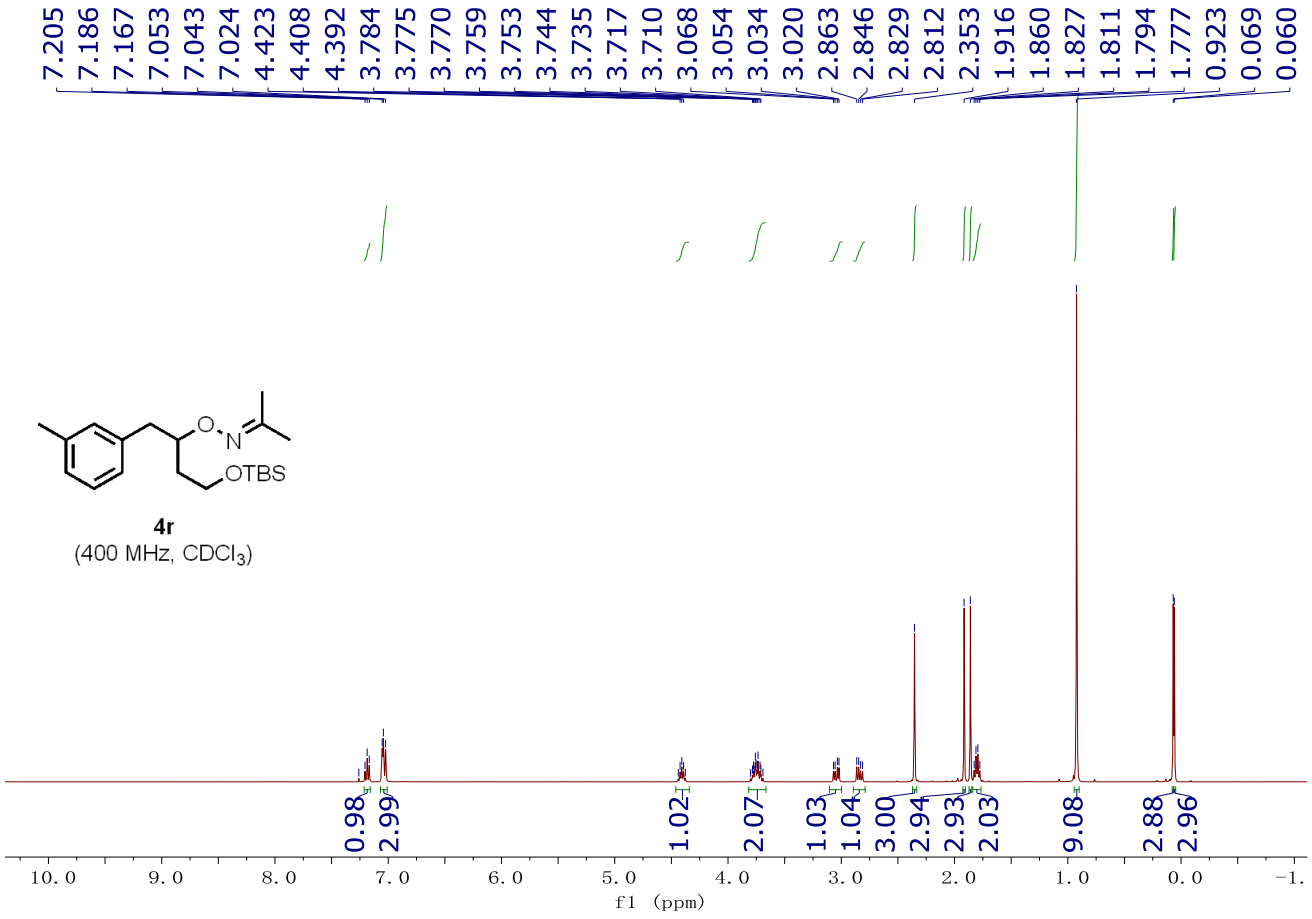

154.35
137.54
137.11
129.13
128.98
125.78
125.36
77.31
77.29
77.00
76.68
37.17
29.57
25.10
21.75
19.37
15.56
O
N
4o
(100 MHz, CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

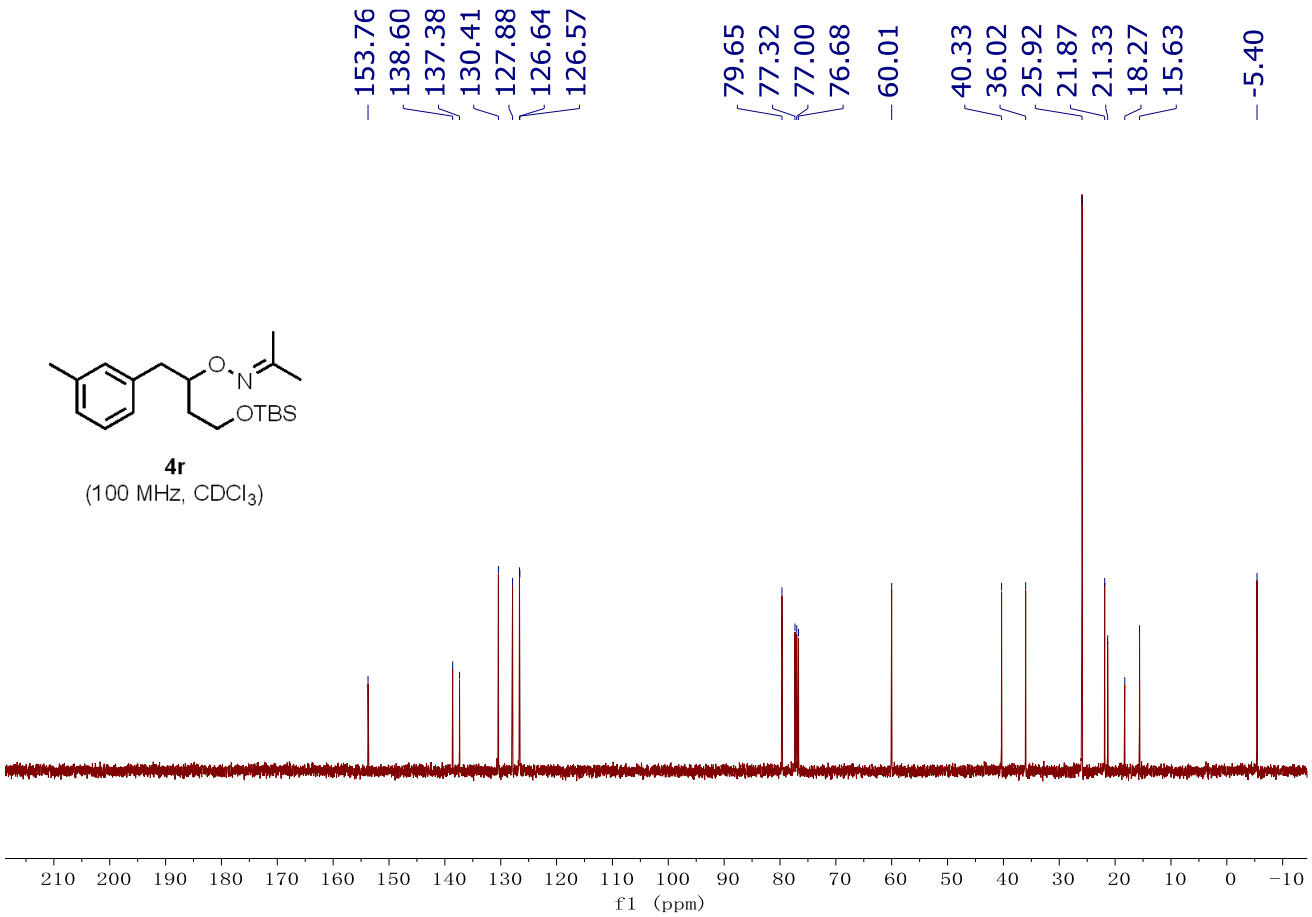

7.192
7.161
7.142
7.124
7.008
6.999
6.980
4.385
4.369
4.353
4.338
4.322
4.307
3.009
2.994
2.975
2.961
2.689
2.672
2.656
2.638
2.305
1.858
1.820
1.183
1.167
-0.000
O
N
4p
(400 MHz, CDCl3)
0.98
2.93
1.00
1.08
1.09
3.09
3.06
3.00
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


153.88
138.64
137.42
130.34
127.90
126.61
126.55
78.86
77.32
77.00
76.68
42.00
21.85
21.30
19.15
15.63
O
N
4p
(100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −2
f1 (ppm)

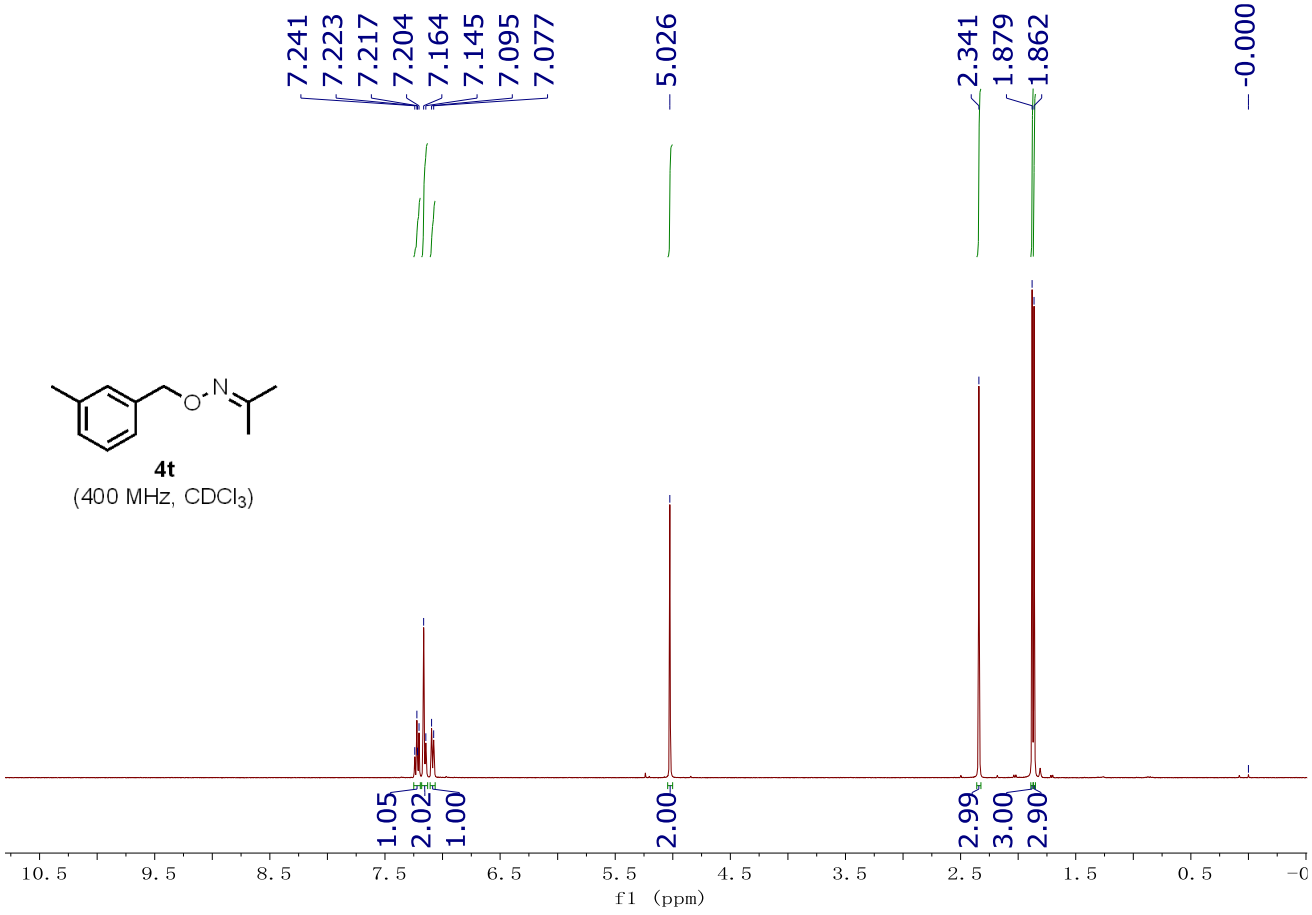

7.156
7.137
7.119
7.005
6.994
6.975
4.223
4.208
4.194
2.968
2.954
2.934
2.920
2.768
2.752
2.734
2.718
2.306
1.861
1.818
1.531
1.518
1.506
1.494
1.482
1.449
1.413
1.317
1.305
1.290
1.273
1.263
1.255
0.880
0.862
0.845
O
N
nBu
4q
(400 MHz, CDCl3)
0.97
2.92
0.99
0.99
0.98
2.91
3.00
2.91
3.08
3.10
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)


153.72
138.90
137.36
130.39
127.84
126.59
126.51
82.82
77.32
77.00
76.68
40.10
32.54
27.68
22.71
21.89
21.33
15.66
14.02
O
N
nBu
4q
(100 MHz, CDCl3)
f1 (ppm)

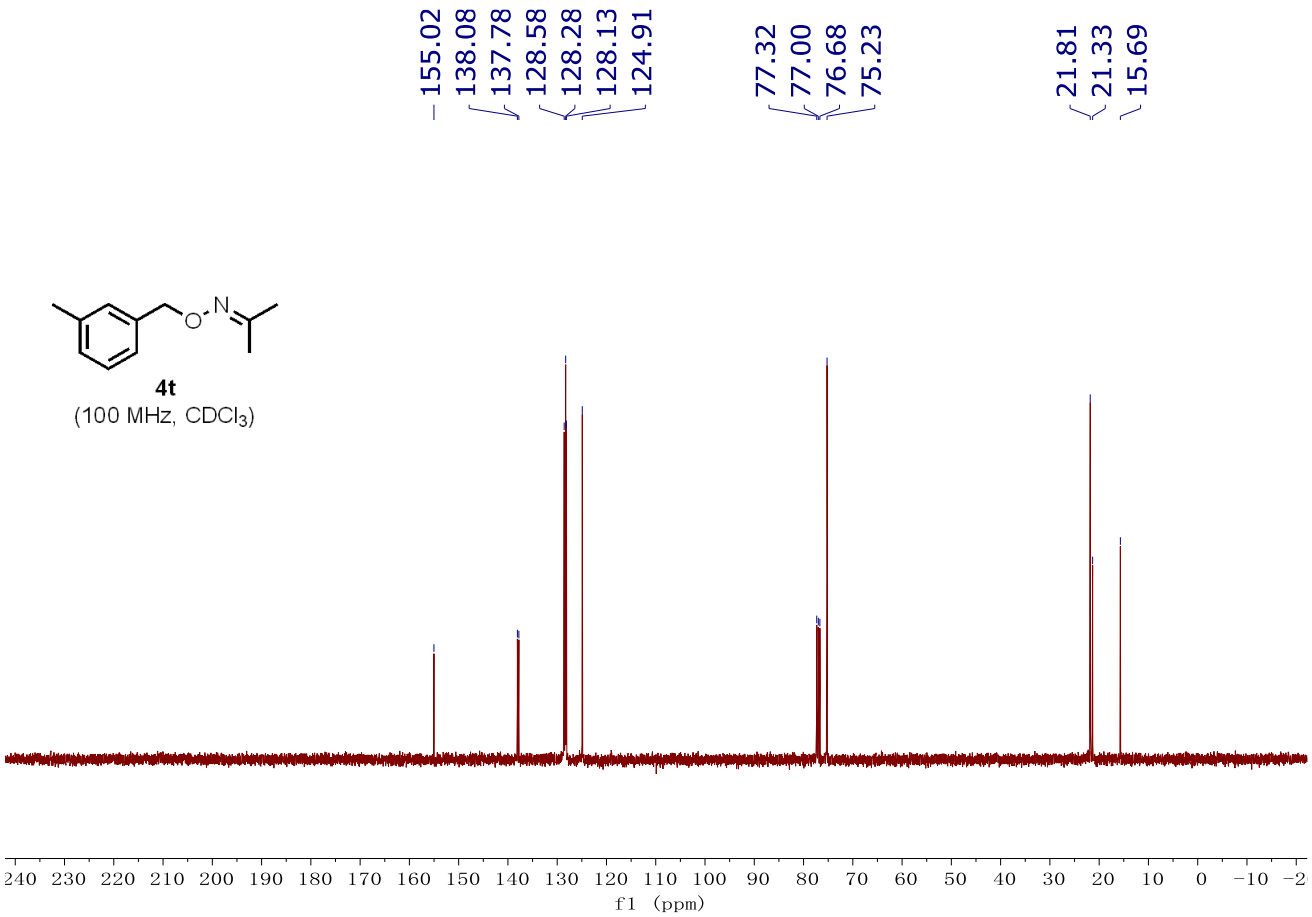

7.205
7.186
7.167
7.053
7.043
7.024
4.423
4.408
4.392
3.784
3.775
3.770
3.759
3.753
3.744
3.735
3.717
3.710
3.068
3.054
3.034
3.020
2.863
2.846
2.829
2.812
2.353
1.916
1.860
1.827
1.811
1.794
1.777
0.923
0.069
0.060
O
N
OTBS
4r
(400 MHz, CDCl3)
0.98
2.99
1.02
2.07
1.03
1.04
3.00
2.94
2.93
2.03
9.08
2.88
2.96
f1 (ppm)

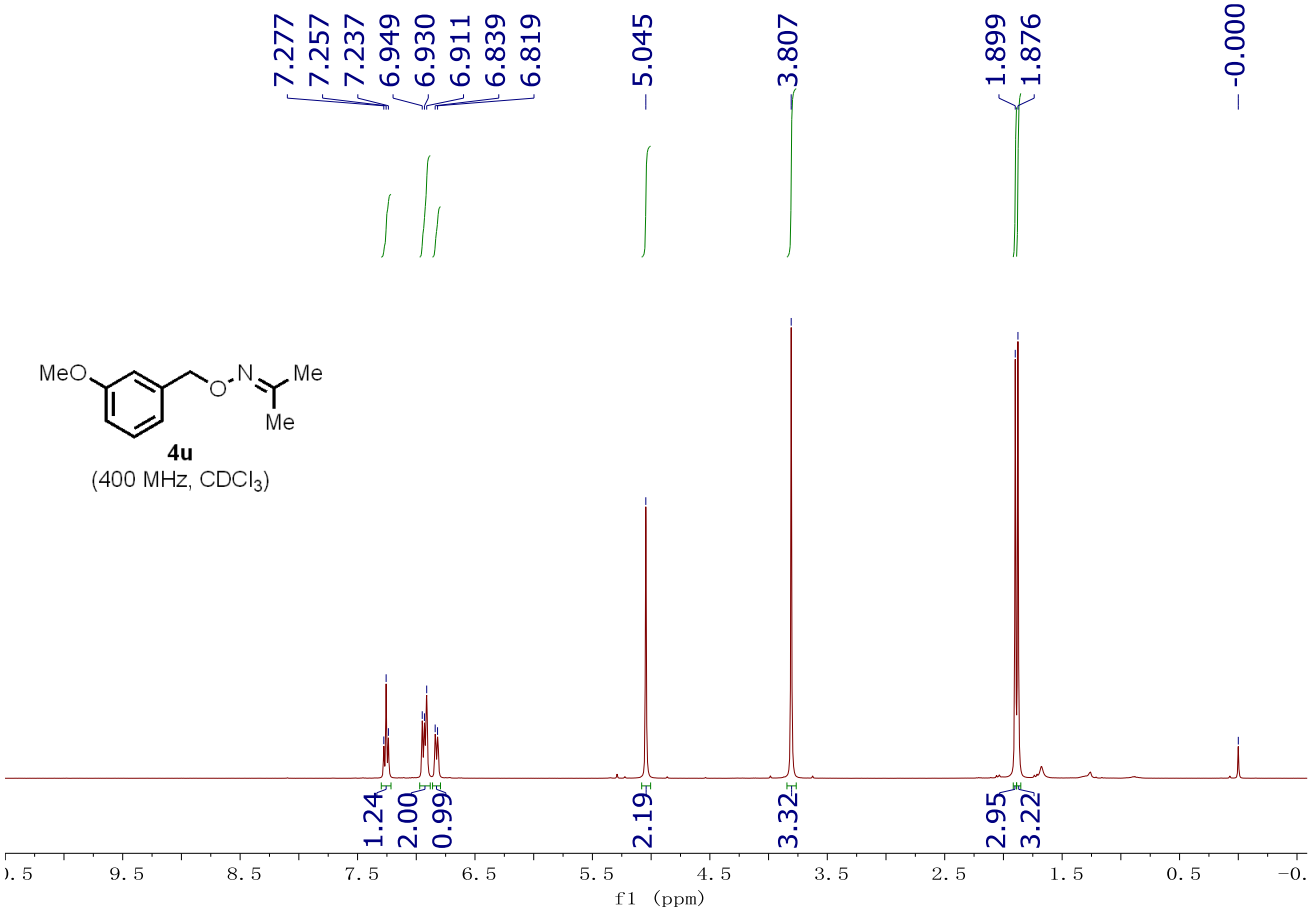


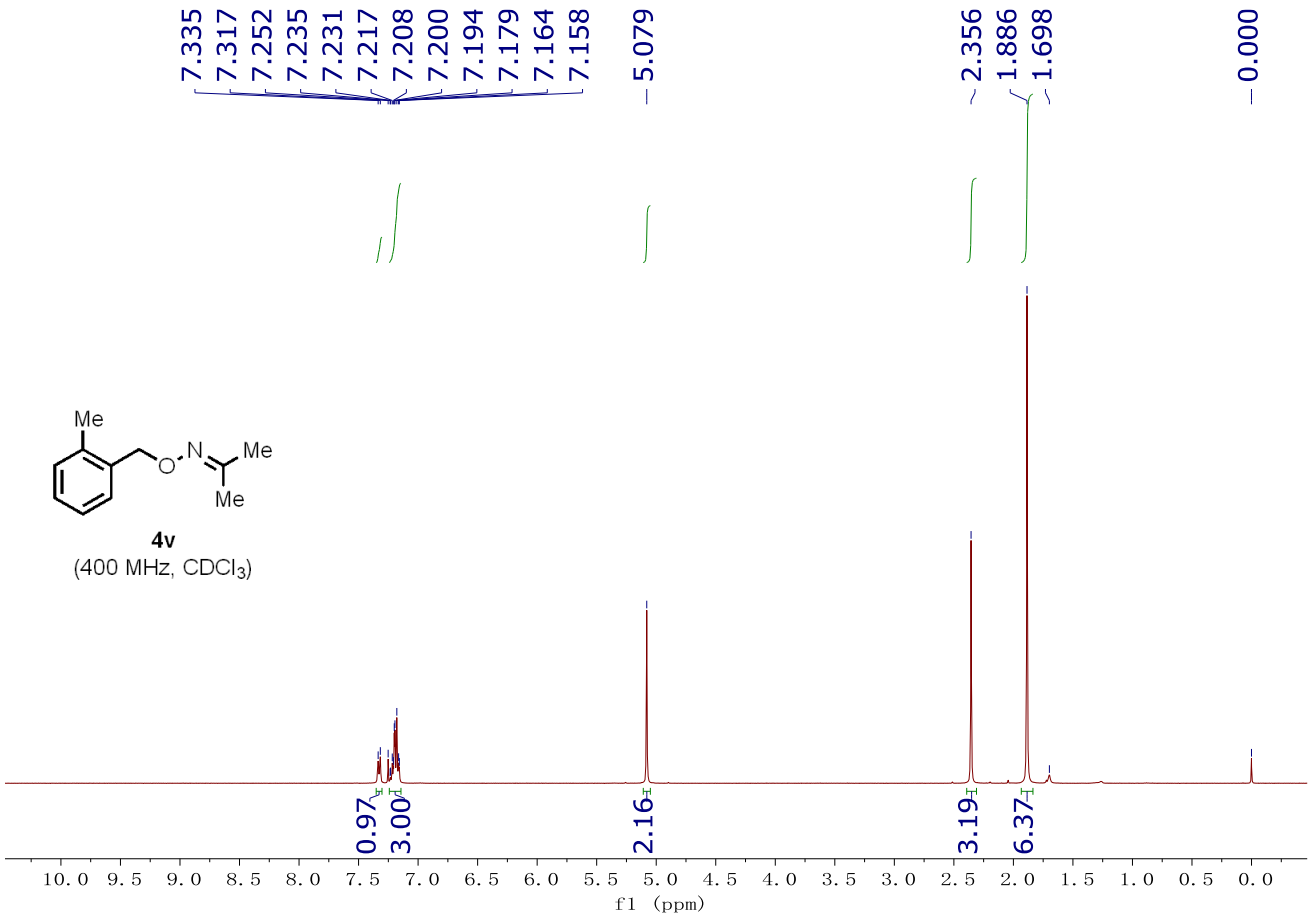
4r
(100 MHz, $CDCl_3$)

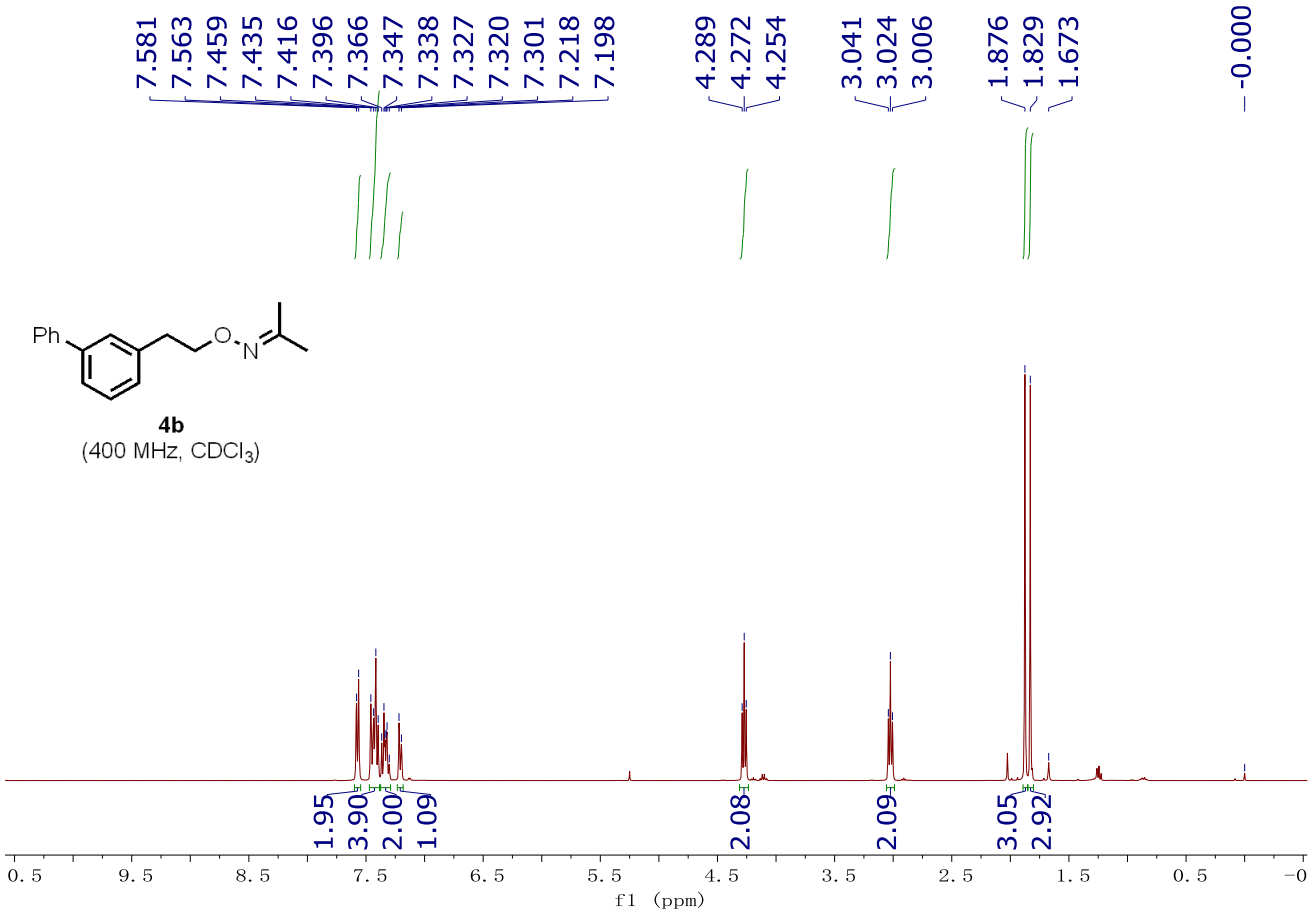


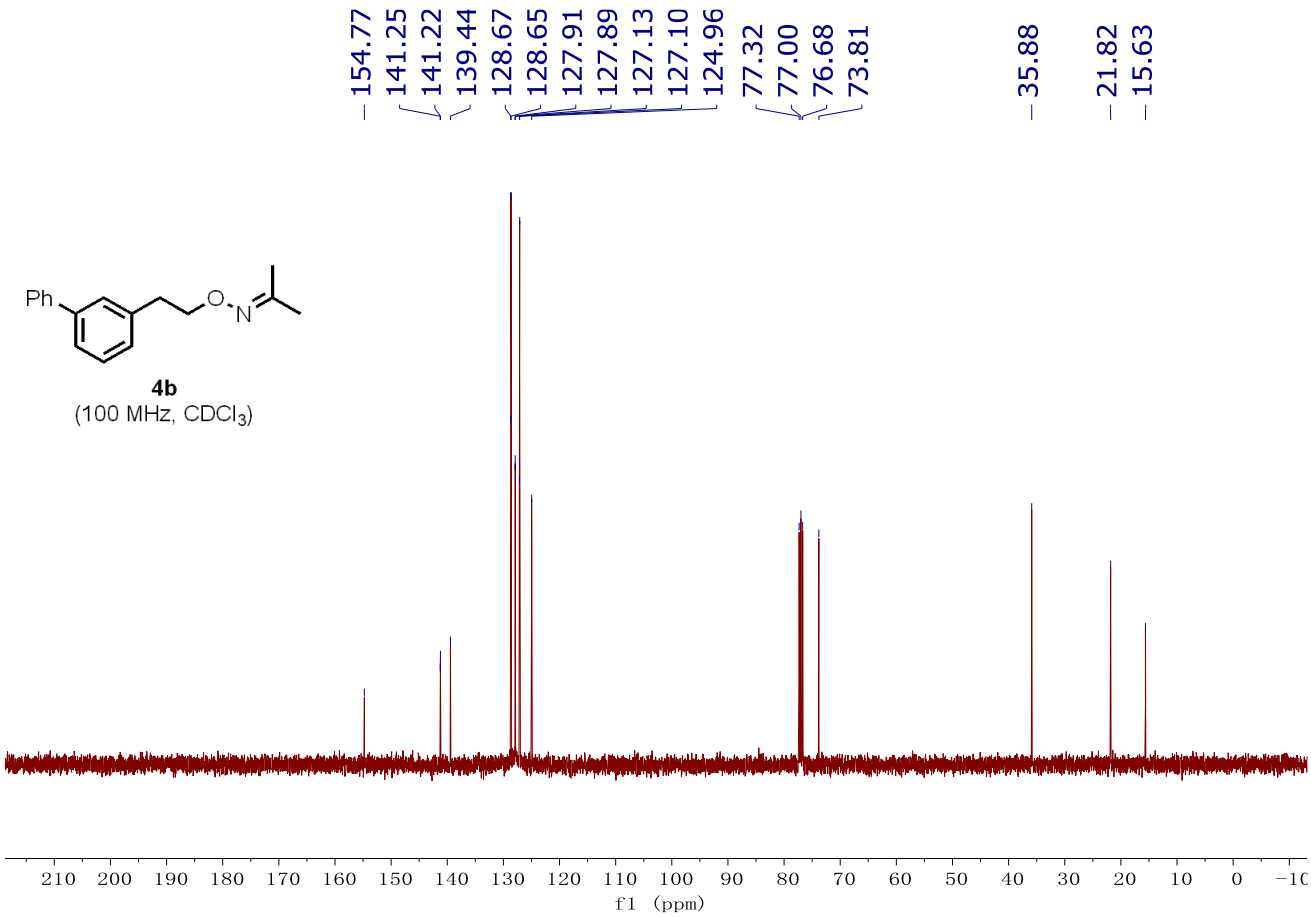
4t
(400 MHz, $CDCl_3$)


155.02
138.08
137.78
128.58
128.28
128.13
124.91
77.32
77.00
76.68
75.23
21.81
21.33
15.69
4t
(100 MHz, CDCl3)
f1 (ppm)

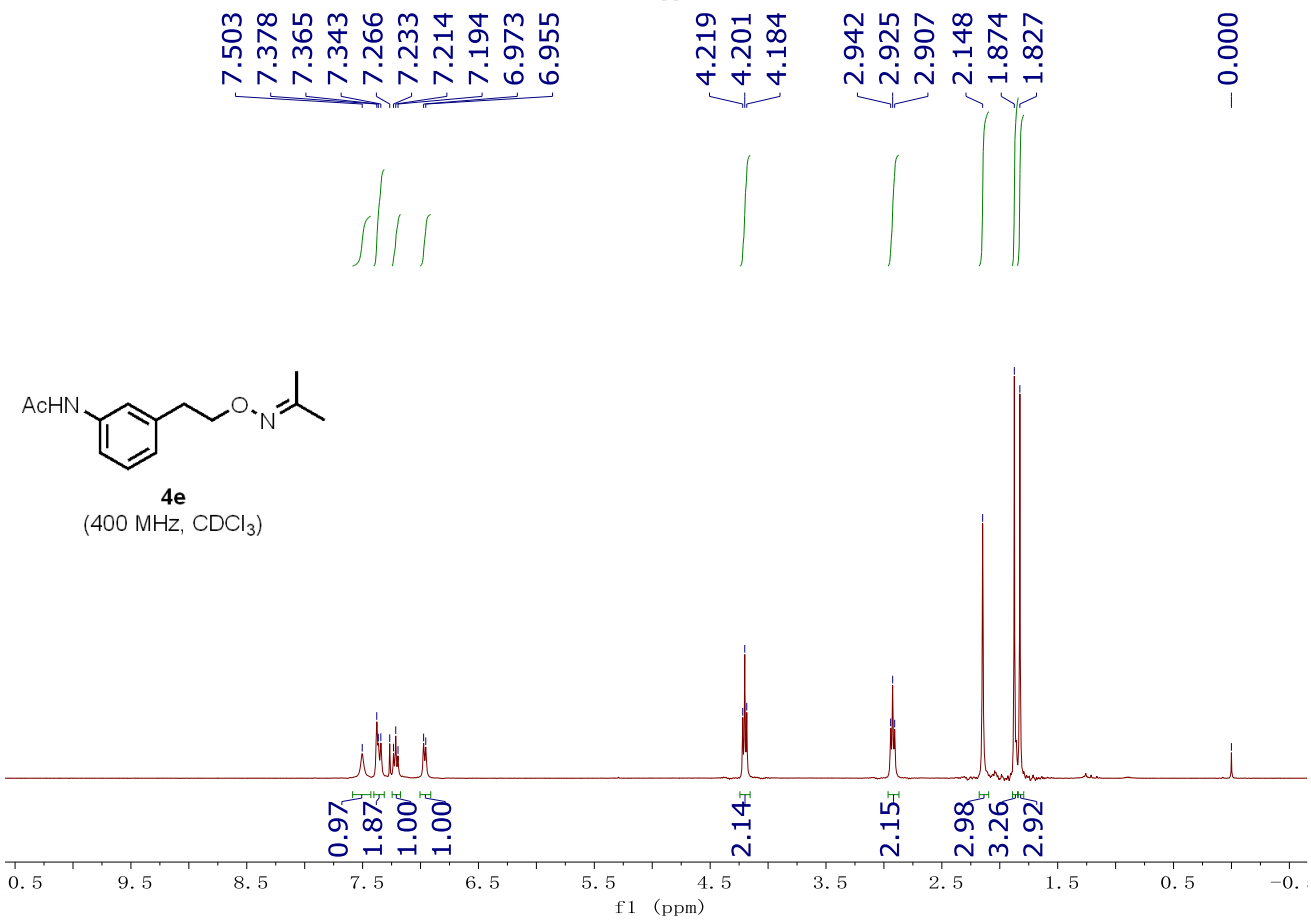

7.277
7.257
7.237
6.949
6.930
6.911
6.839
6.819
5.045
3.807
1.899
1.876
-0.000
MeO
Me
Me
4u
(400 MHz, CDCl3)
1.24
2.00
0.99
2.19
3.32
2.95
3.22
f1 (ppm)


7.335
7.317
7.252
7.235
7.231
7.217
7.208
7.200
7.194
7.179
7.164
7.158
5.079
2.356
1.886
1.698
0.000
Me
N
O
Me
Me
4v
(400 MHz, CDCl3)
0.97
3.00
2.16
3.19
6.37
f1 (ppm)

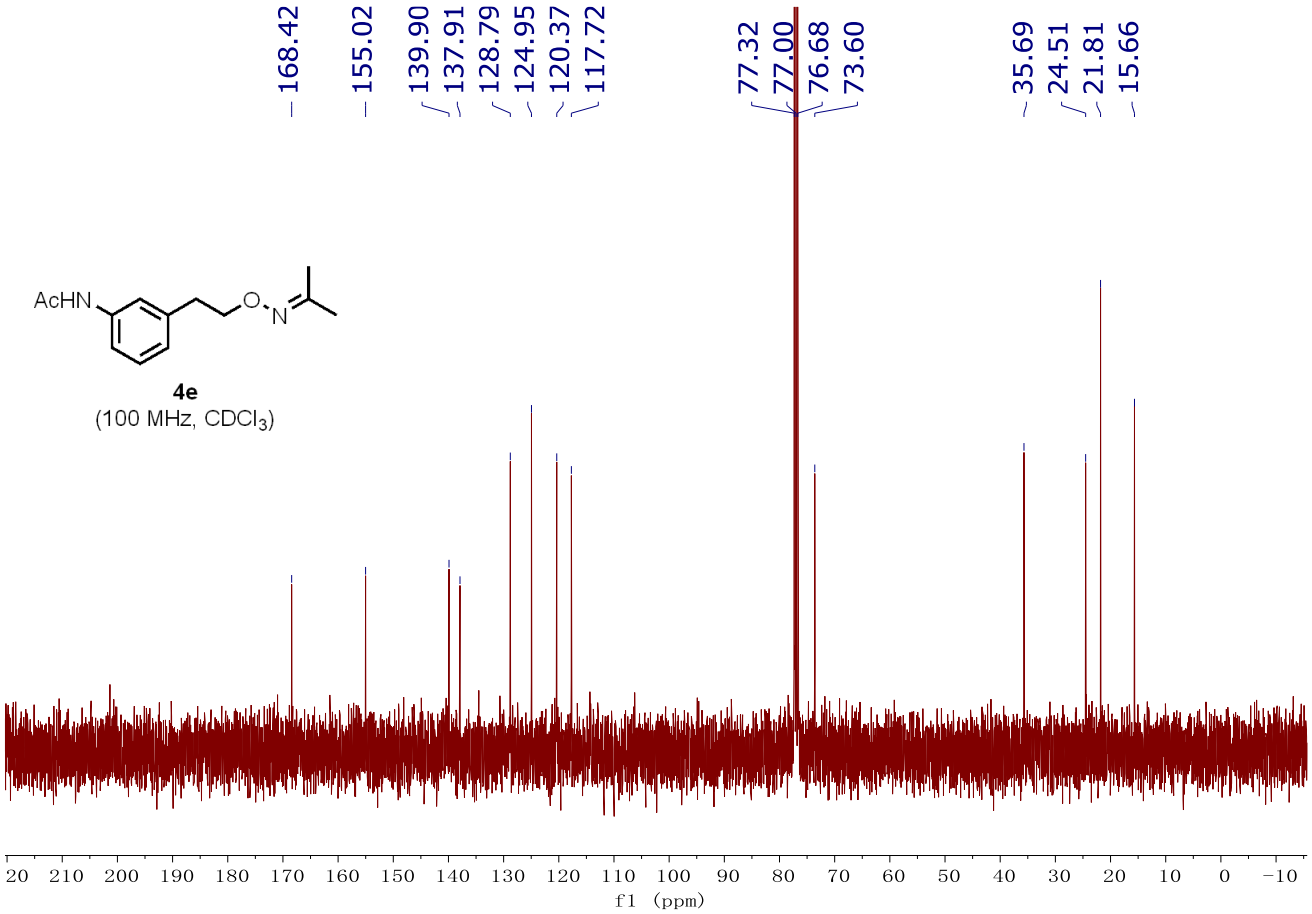

7.581
7.563
7.459
7.435
7.416
7.396
7.366
7.347
7.338
7.327
7.320
7.301
7.218
7.198
4.289
4.272
4.254
3.041
3.024
3.006
1.876
1.829
1.673
-0.000
Ph
O
N
4b
(400 MHz, CDCl3)
1.95
3.90
2.00
1.09
2.08
2.09
3.05
2.92
f1 (ppm)

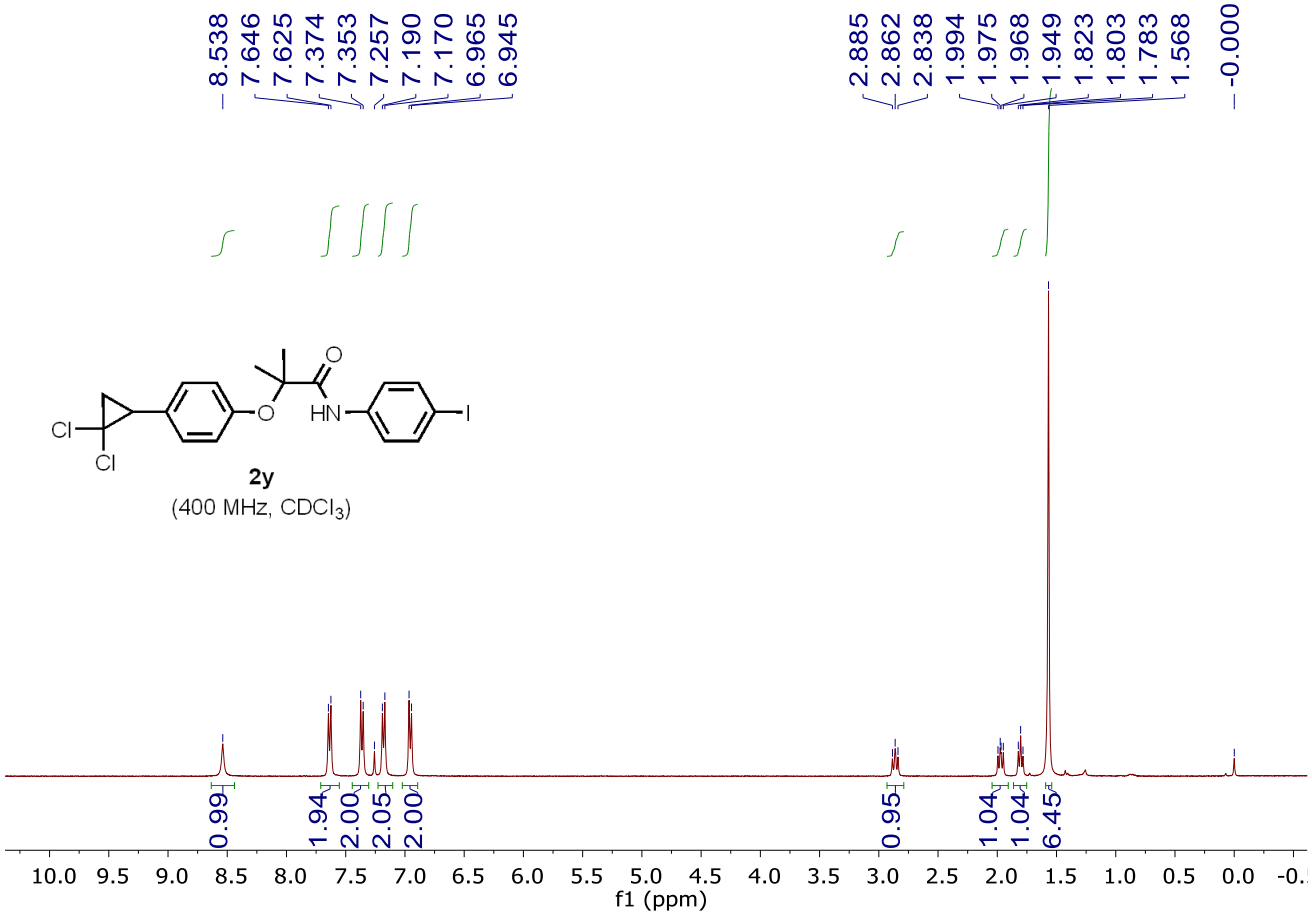


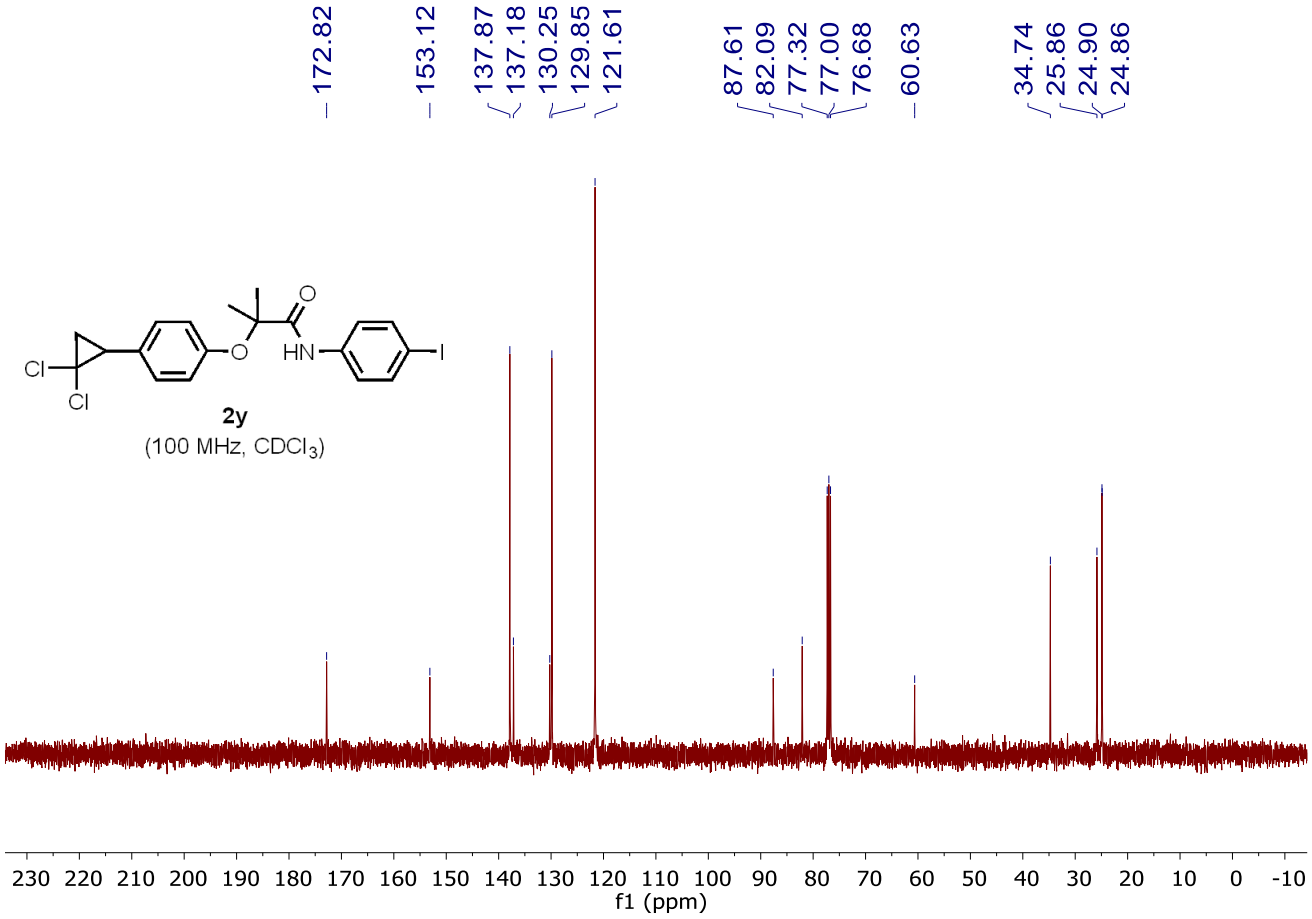
4b
(100 MHz, $CDCl_3$)

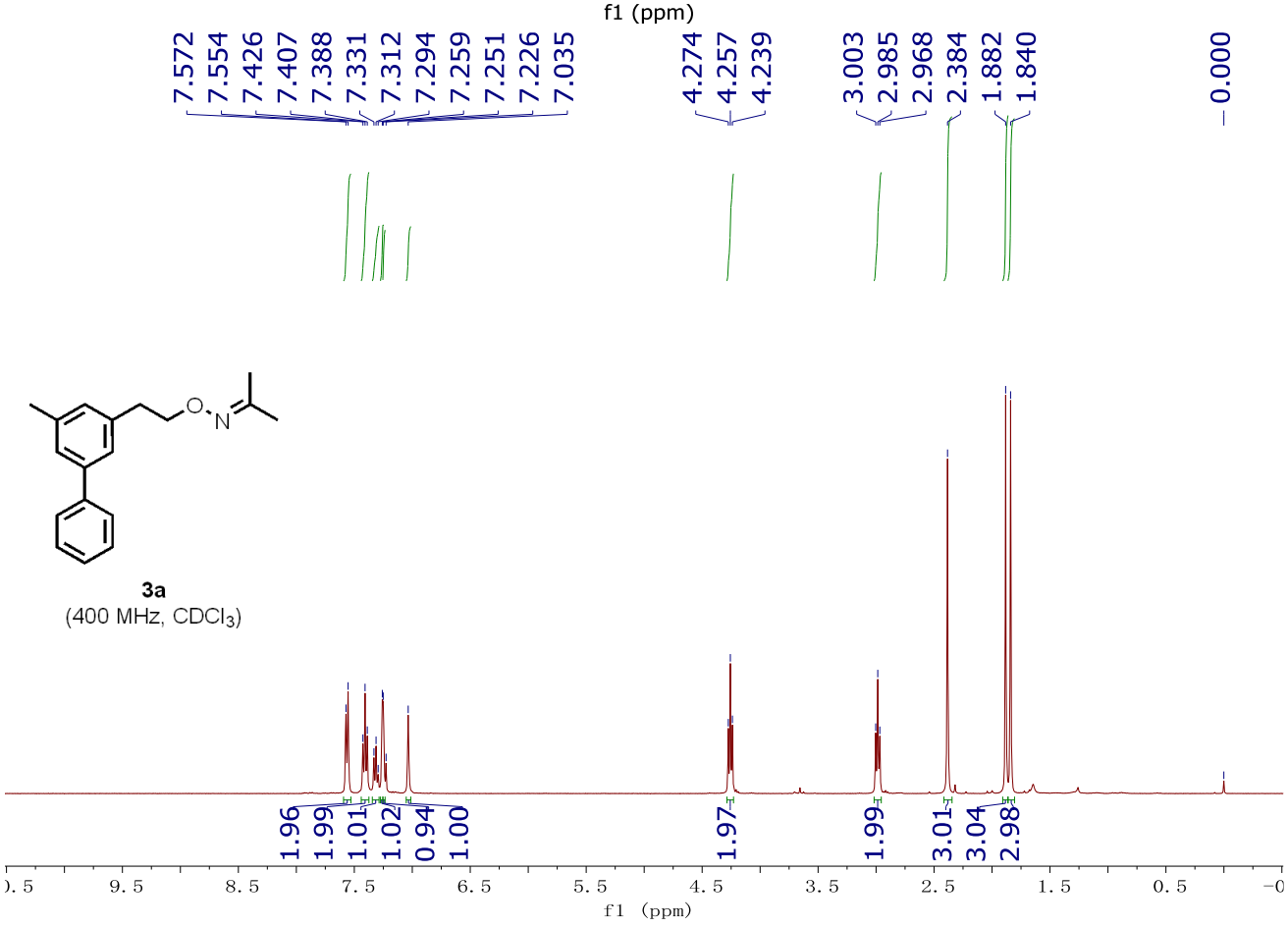


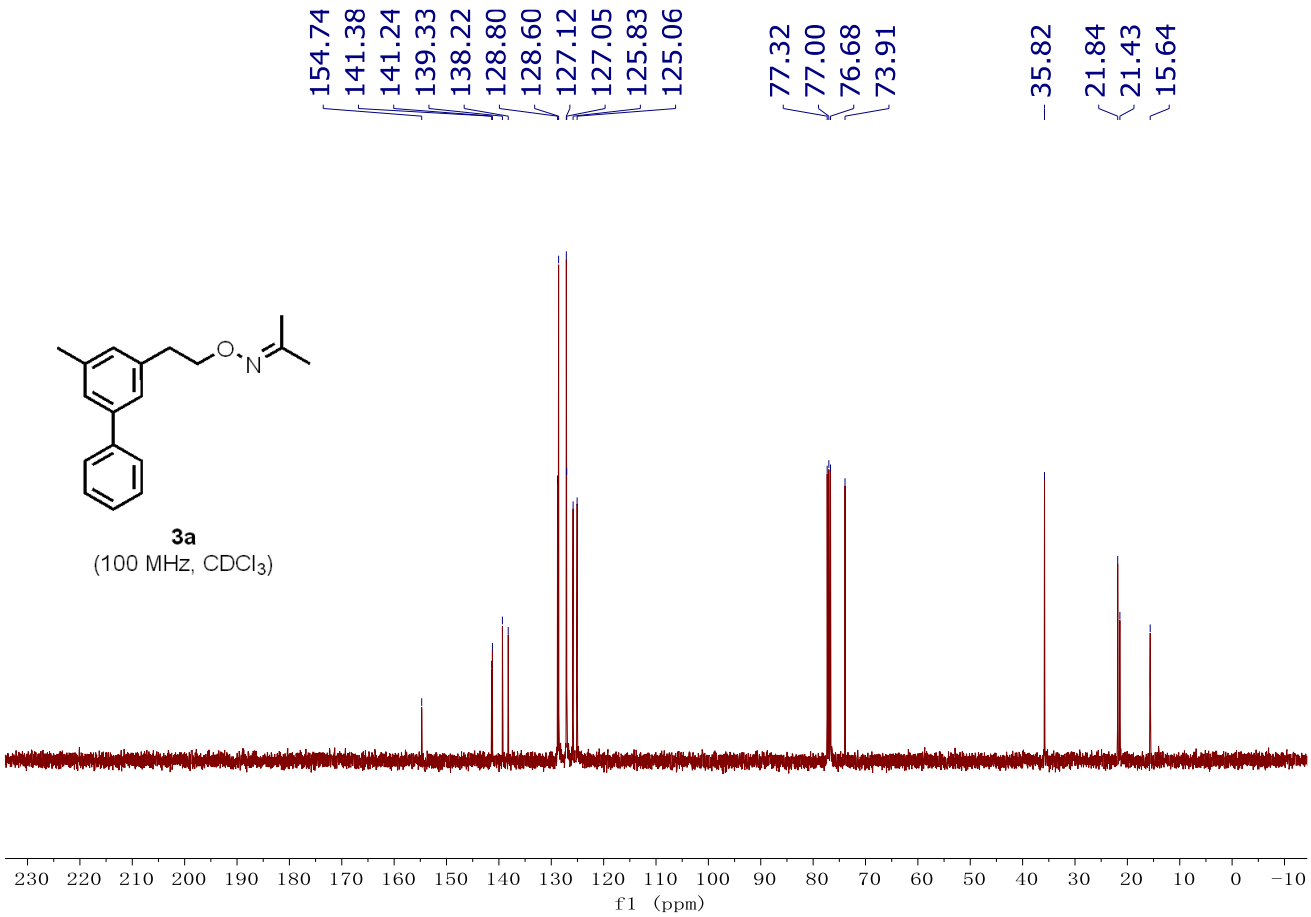
4e
(400 MHz, $CDCl_3$)

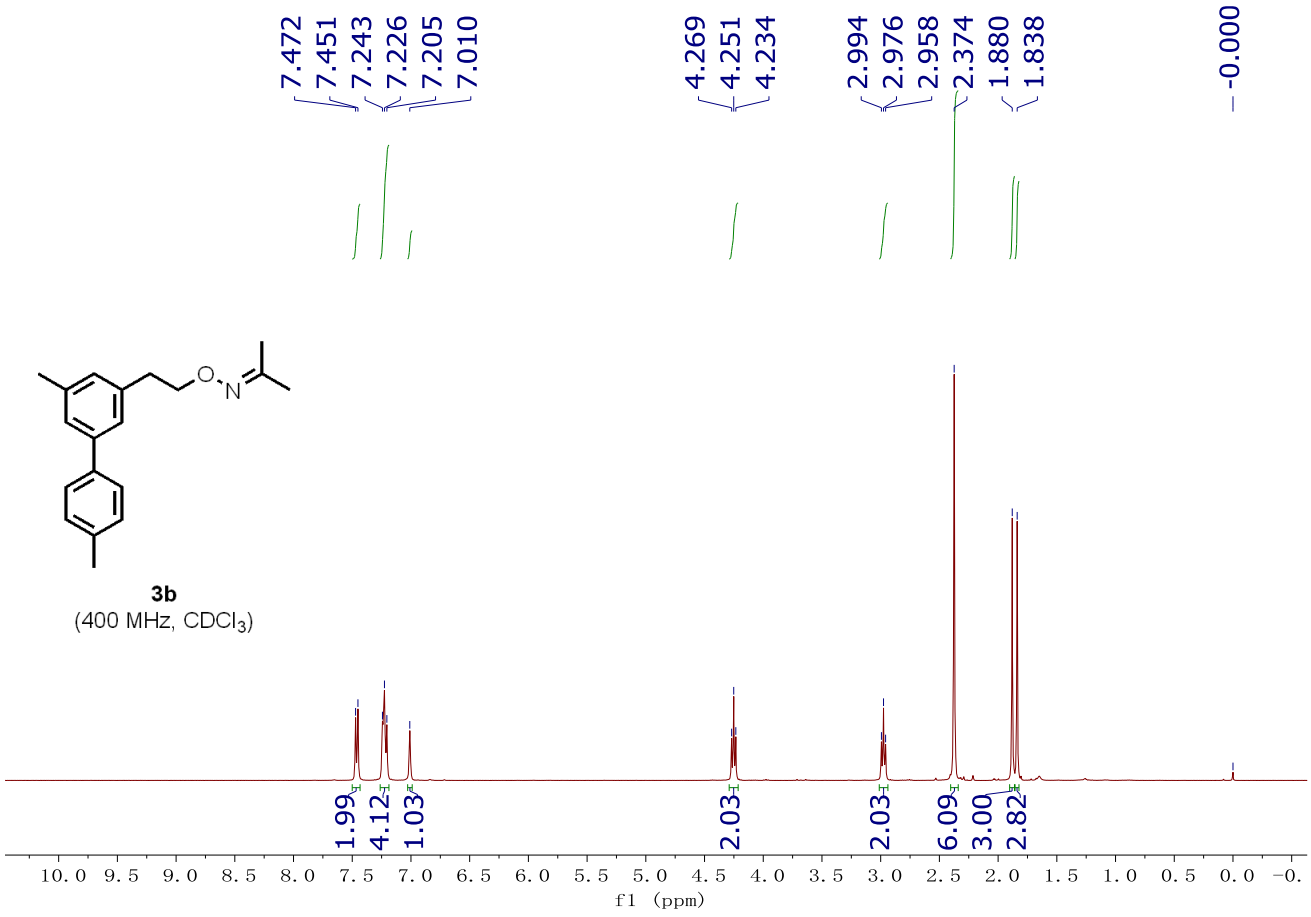

168.42
155.02
139.90
137.91
128.79
124.95
120.37
117.72
77.32
77.00
76.68
73.60
35.69
24.51
21.81
15.66
AcHN
O
N
4e
(100 MHz, CDCl3)
f1 (ppm)

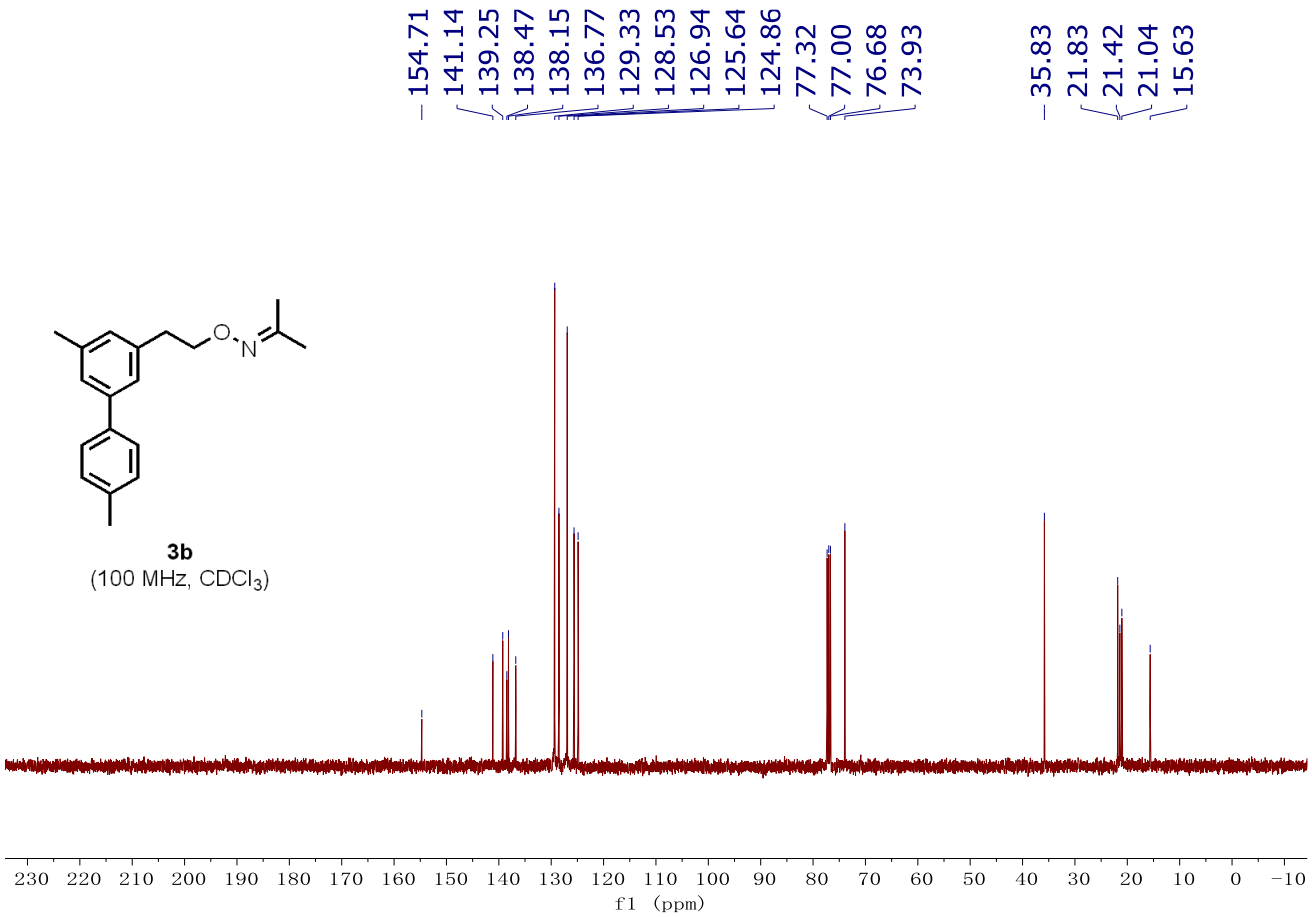

8.538
7.646
7.625
7.374
7.353
7.257
7.190
7.170
6.965
6.945
2.885
2.862
2.838
1.994
1.975
1.968
1.949
1.823
1.803
1.783
1.568
-0.000
Cl
Cl
O
HN
O
I
2y
(400 MHz, CDCl3)
0.99
1.94
2.00
2.05
2.00
0.95
1.04
1.04
6.45
f1 (ppm)

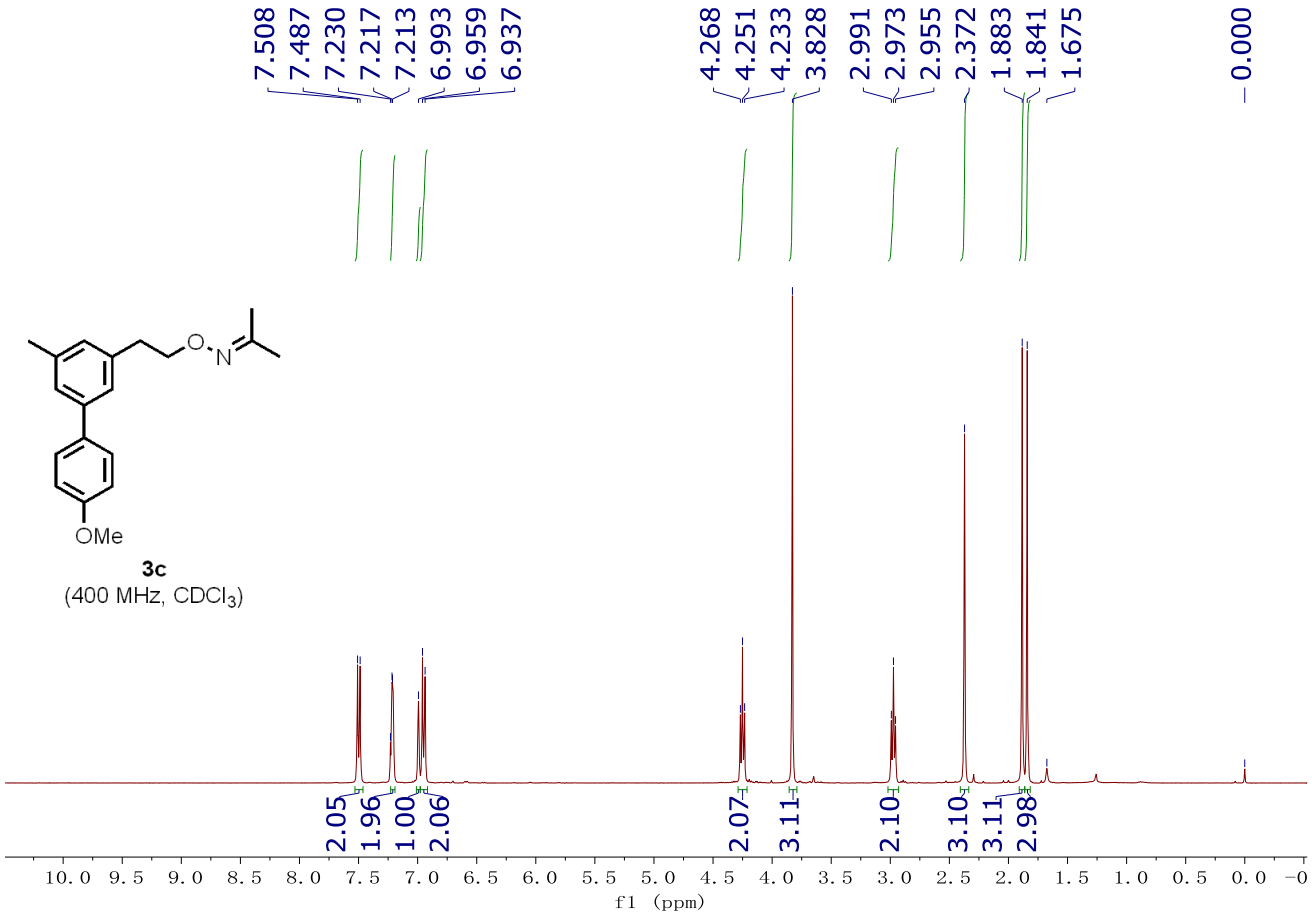

172.82
153.12
137.87
137.18
130.25
129.85
121.61
87.61
82.09
77.32
77.00
76.68
60.63
34.74
25.86
24.90
24.86
Cl
Cl
O
HN
I
O
2y
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

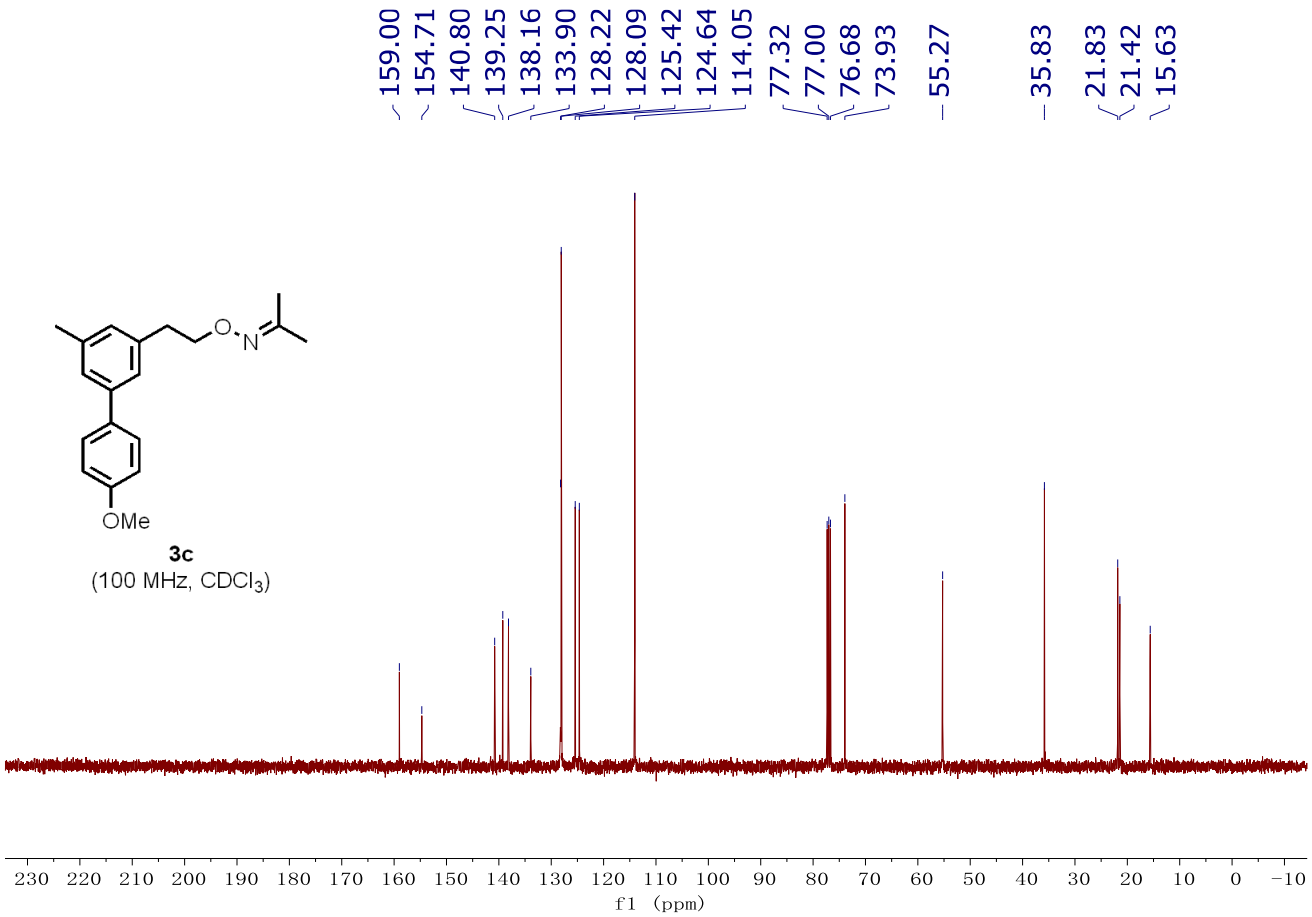

7.572
7.554
7.426
7.407
7.388
7.331
7.312
7.294
7.259
7.251
7.226
7.035
4.274
4.257
4.239
3.003
2.985
2.968
2.384
1.882
1.840
0.000
O
N
3a
(400 MHz, CDCl3)
1.96
1.99
1.01
1.02
0.94
1.00
1.97
1.99
3.01
3.04
2.98
f1 (ppm)

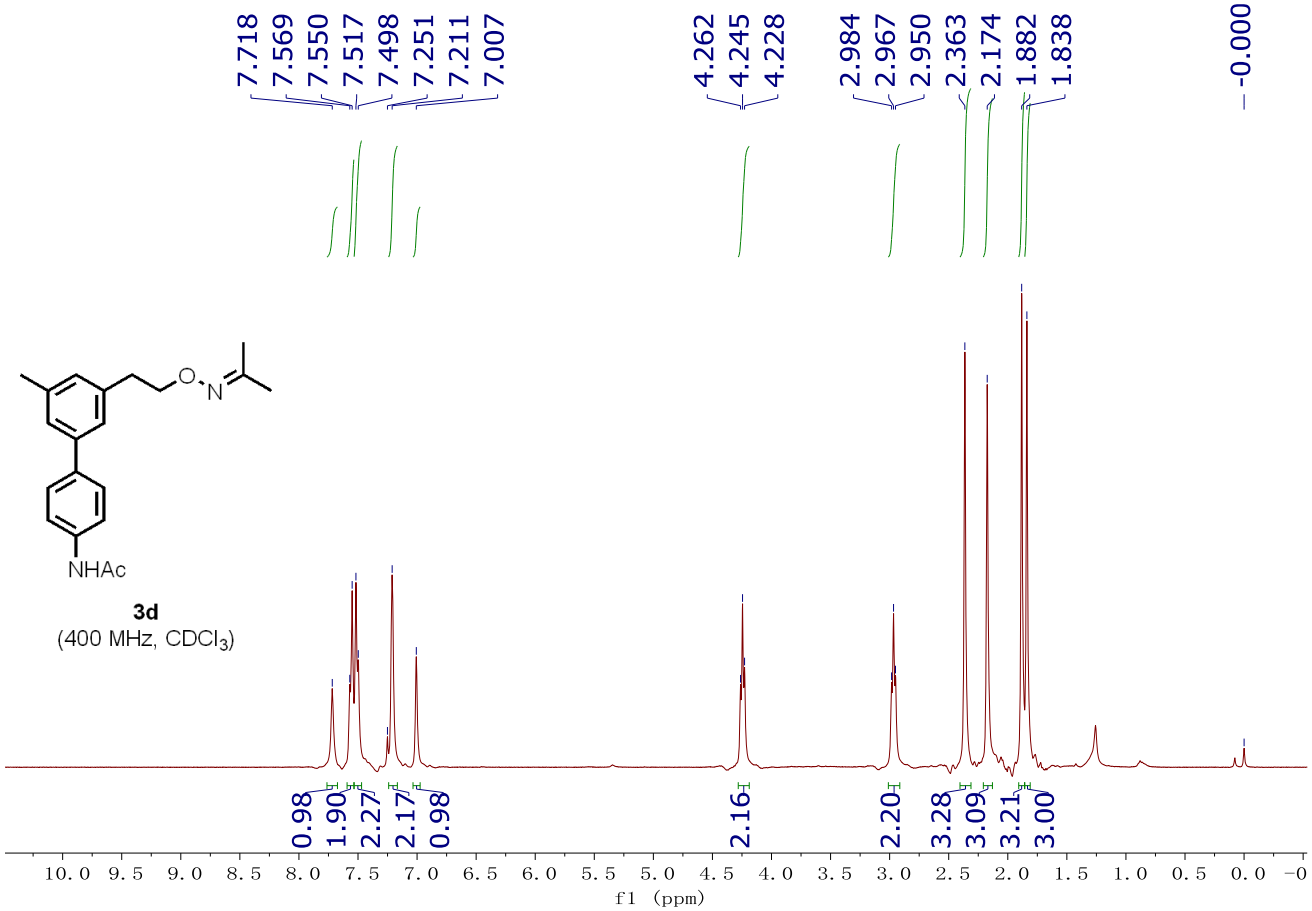

154.74
141.38
141.24
139.33
138.22
128.80
128.60
127.12
127.05
125.83
125.06
77.32
77.00
76.68
73.91
35.82
21.84
21.43
15.64
O
N
3a
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

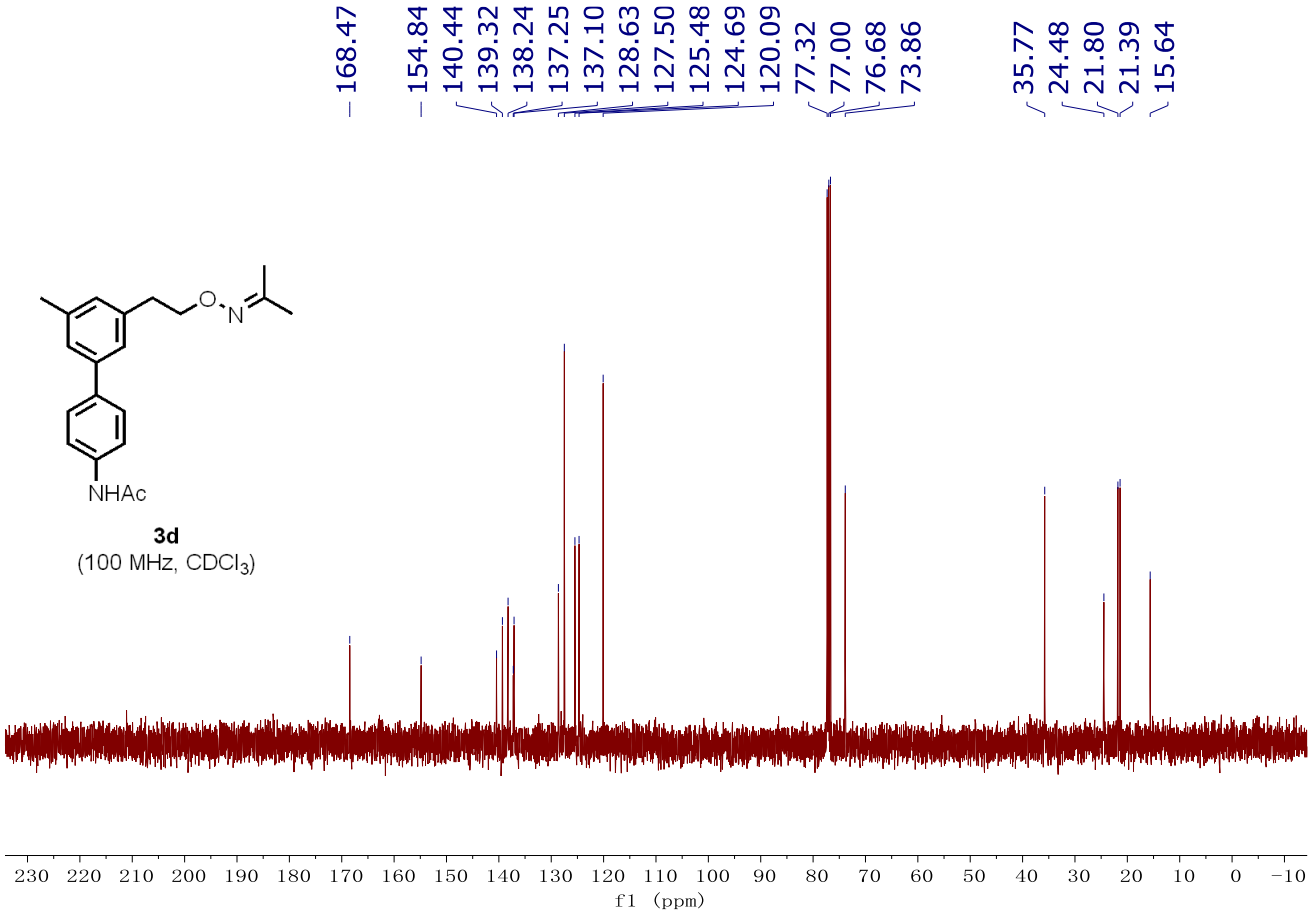

7.472
7.451
7.243
7.226
7.205
7.010
4.269
4.251
4.234
2.994
2.976
2.958
2.374
1.880
1.838
-0.000
O
N
3b
(400 MHz, CDCl3)
1.99
4.12
1.03
2.03
2.03
6.09
3.00
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

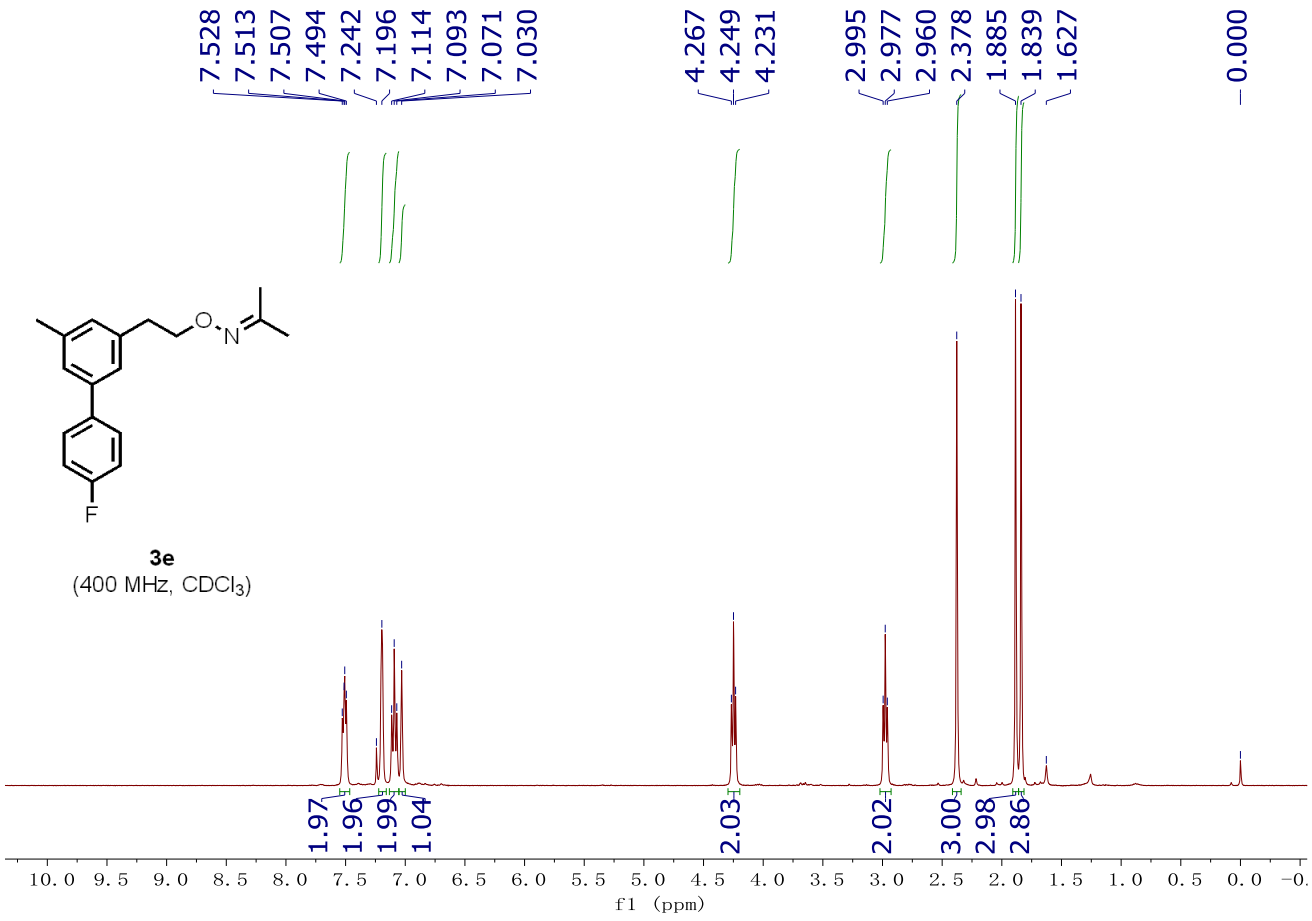

154.71
141.14
139.25
138.47
138.15
136.77
129.33
128.53
126.94
125.64
124.86
77.32
77.00
76.68
73.93
35.83
21.83
21.42
21.04
15.63
3b
(100 MHz, CDCl3)
f1 (ppm)

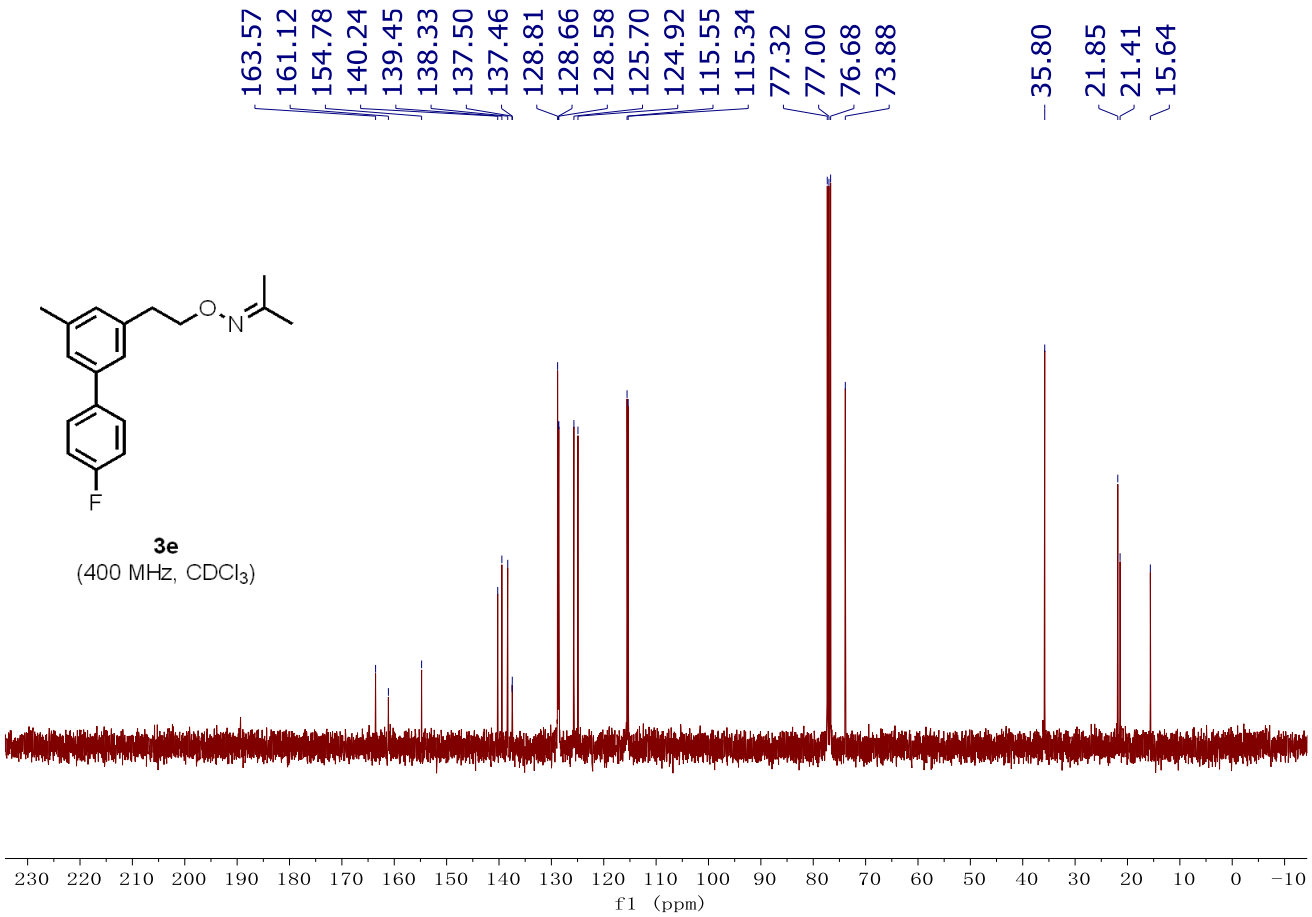

7.508
7.487
7.230
7.217
7.213
6.993
6.959
6.937
4.268
4.251
4.233
3.828
2.991
2.973
2.955
2.372
1.883
1.841
1.675
0.000
OMe
3c
(400 MHz, CDCl3)
2.05
1.96
1.00
2.06
2.07
3.11
2.10
3.10
3.11
2.98
f1 (ppm)

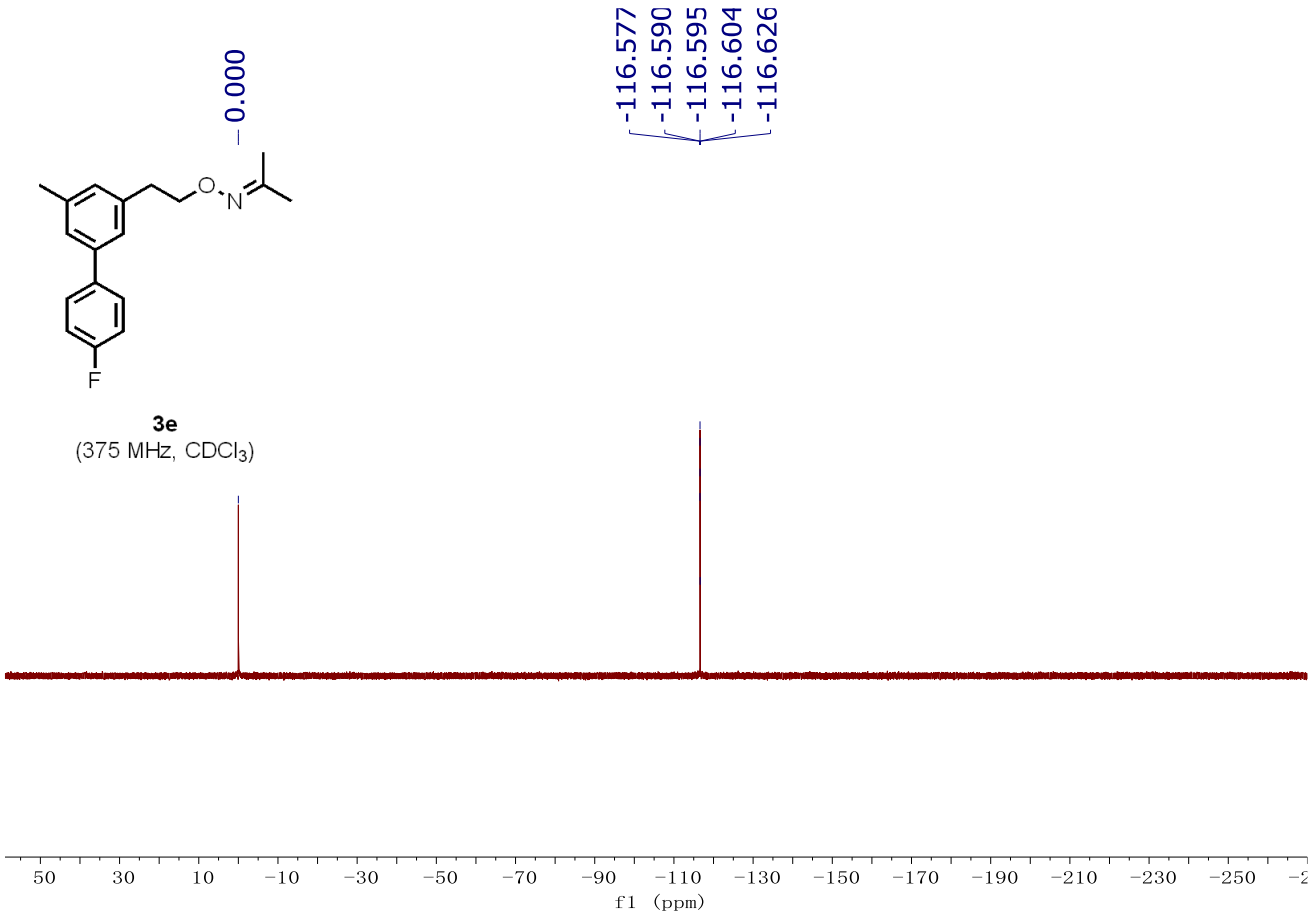

159.00
154.71
140.80
139.25
138.16
133.90
128.22
128.09
125.42
124.64
114.05
77.32
77.00
76.68
73.93
55.27
35.83
21.83
21.42
15.63
OMe
3c
(100 MHz, CDCl3)
f1 (ppm)

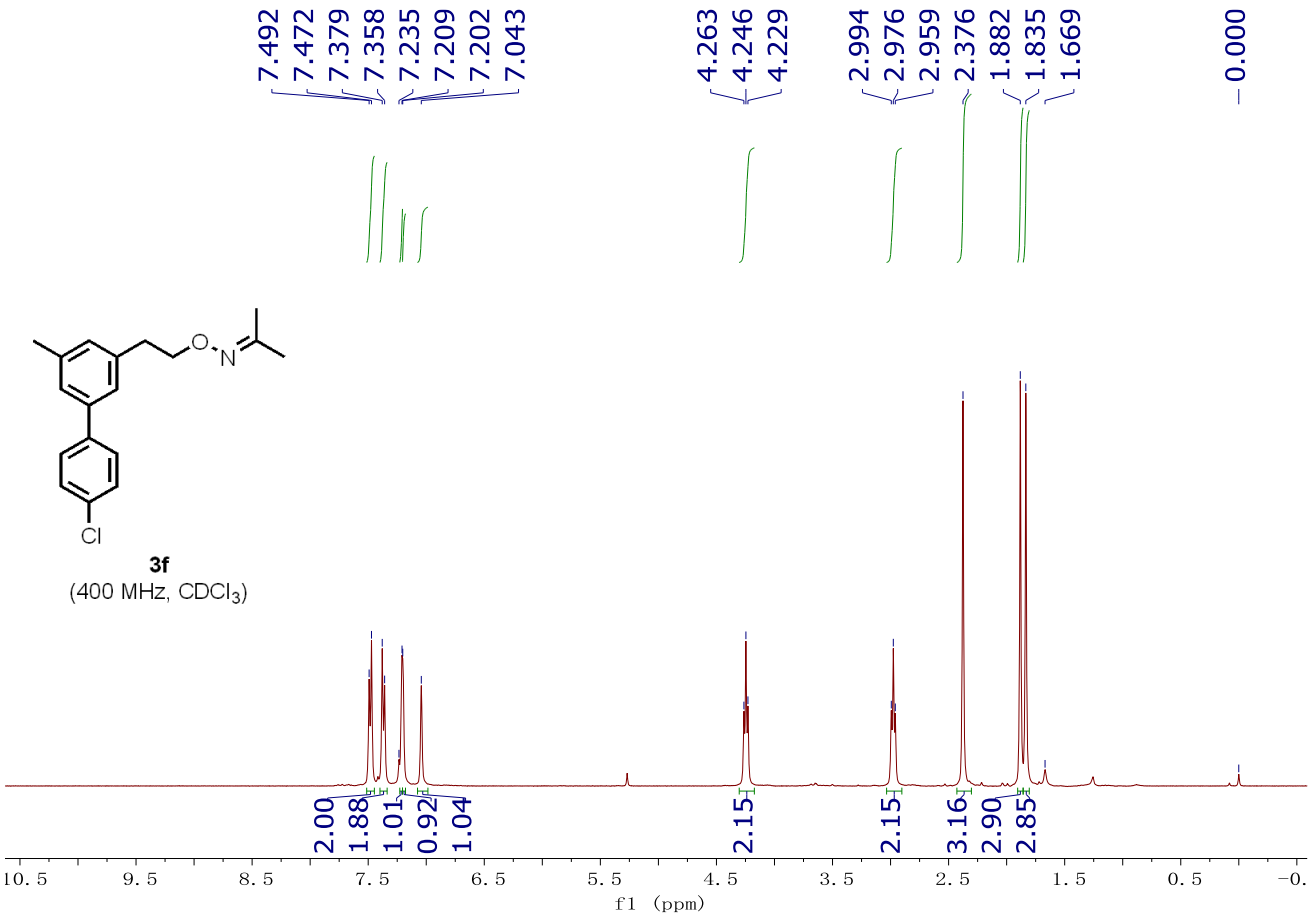

7.718
7.569
7.550
7.517
7.498
7.251
7.211
7.007
4.262
4.245
4.228
2.984
2.967
2.950
2.363
2.174
1.882
1.838
-0.000
NHAc
3d
(400 MHz, CDCl3)
0.98
1.90
2.27
2.17
0.98
2.16
2.20
3.28
3.09
3.21
3.00
f1 (ppm)

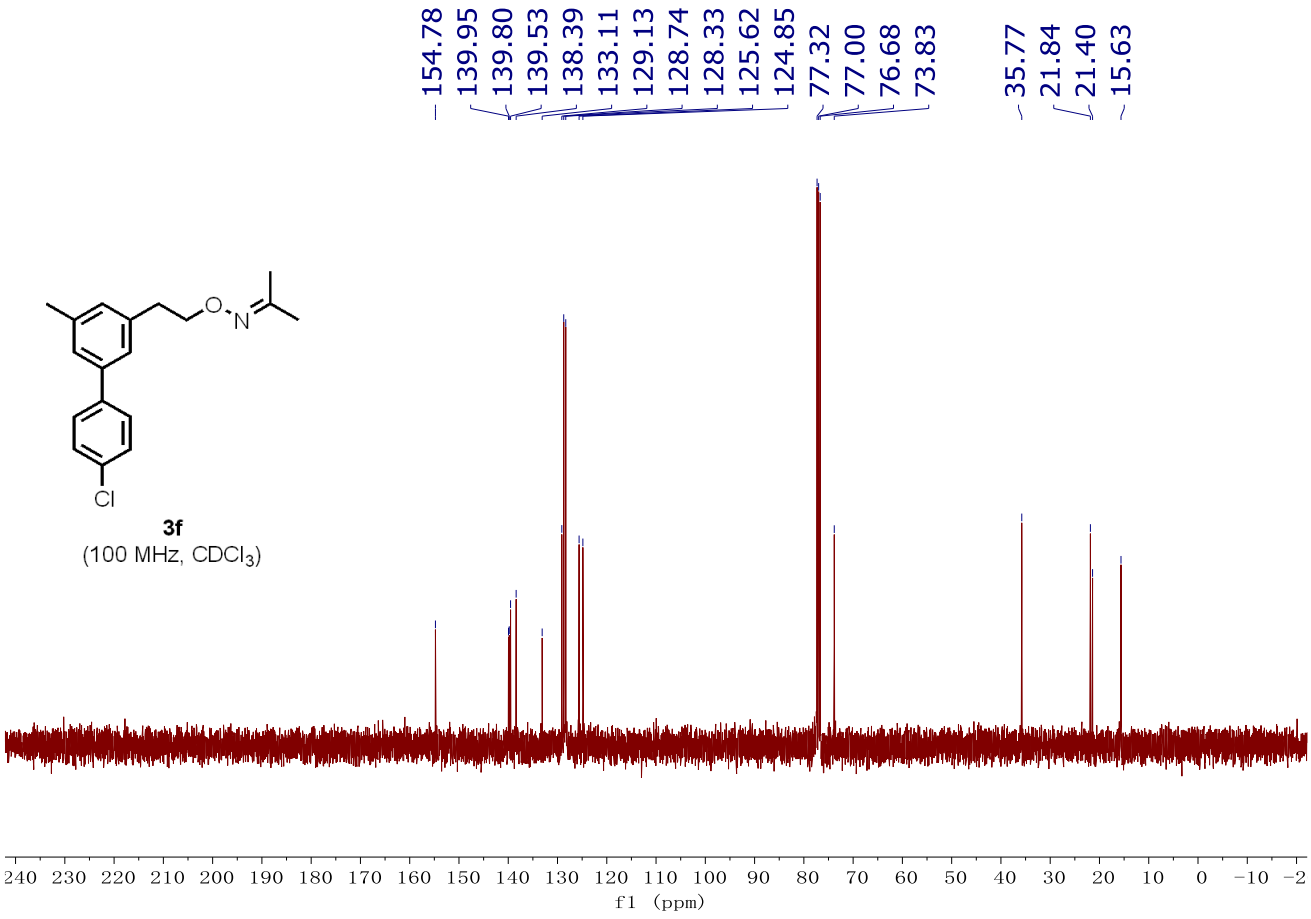

168.47
154.84
140.44
139.32
138.24
137.25
137.10
128.63
127.50
125.48
124.69
120.09
77.32
77.00
76.68
73.86
35.77
24.48
21.80
21.39
15.64
O
N
NHAc
3d
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

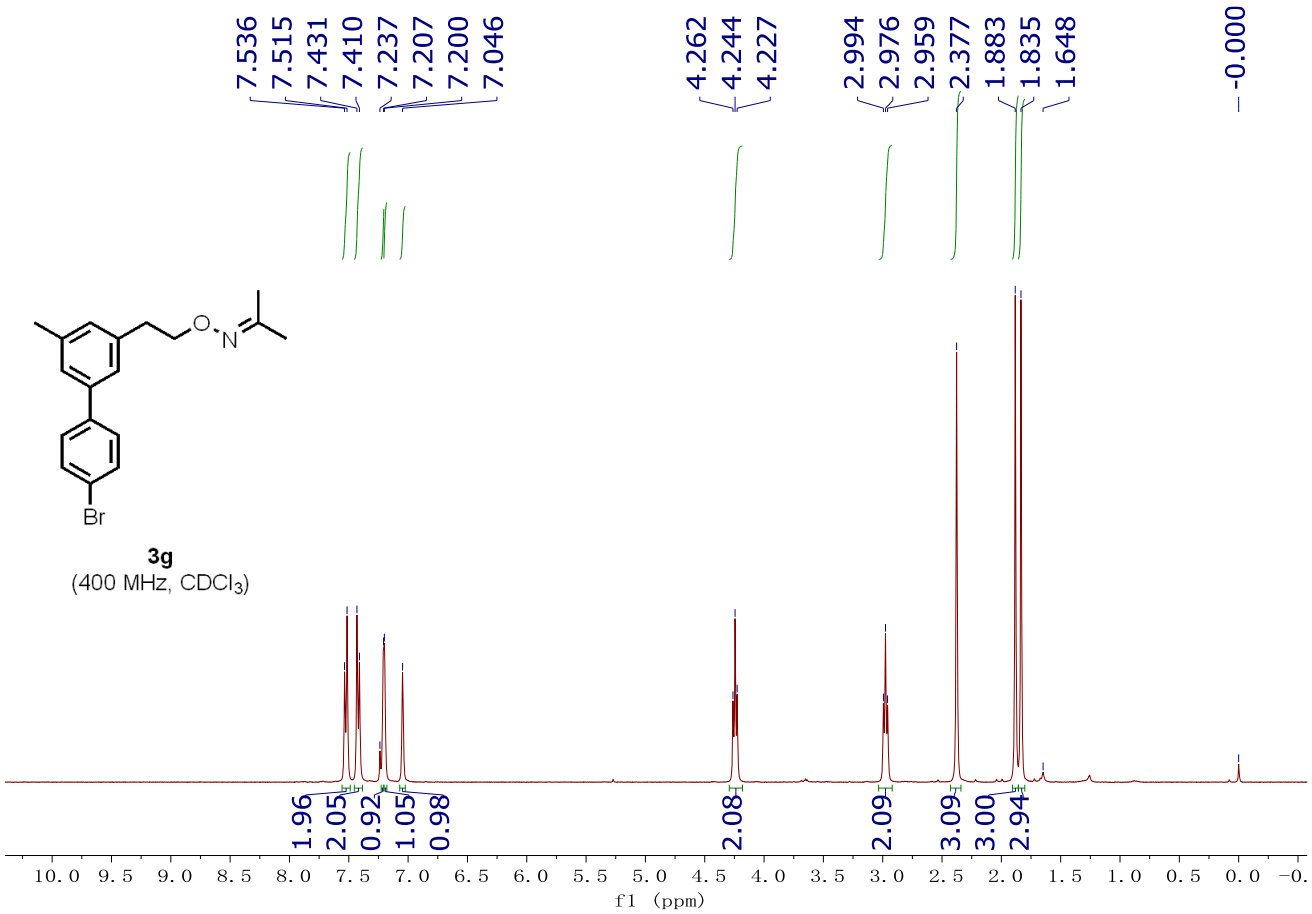

7.528
7.513
7.507
7.494
7.242
7.196
7.114
7.093
7.071
7.030
4.267
4.249
4.231
2.995
2.977
2.960
2.378
1.885
1.839
1.627
0.000
O
N
F
3e
(400 MHz, CDCl3)
1.97
1.96
1.99
1.04
2.03
2.02
3.00
2.98
2.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

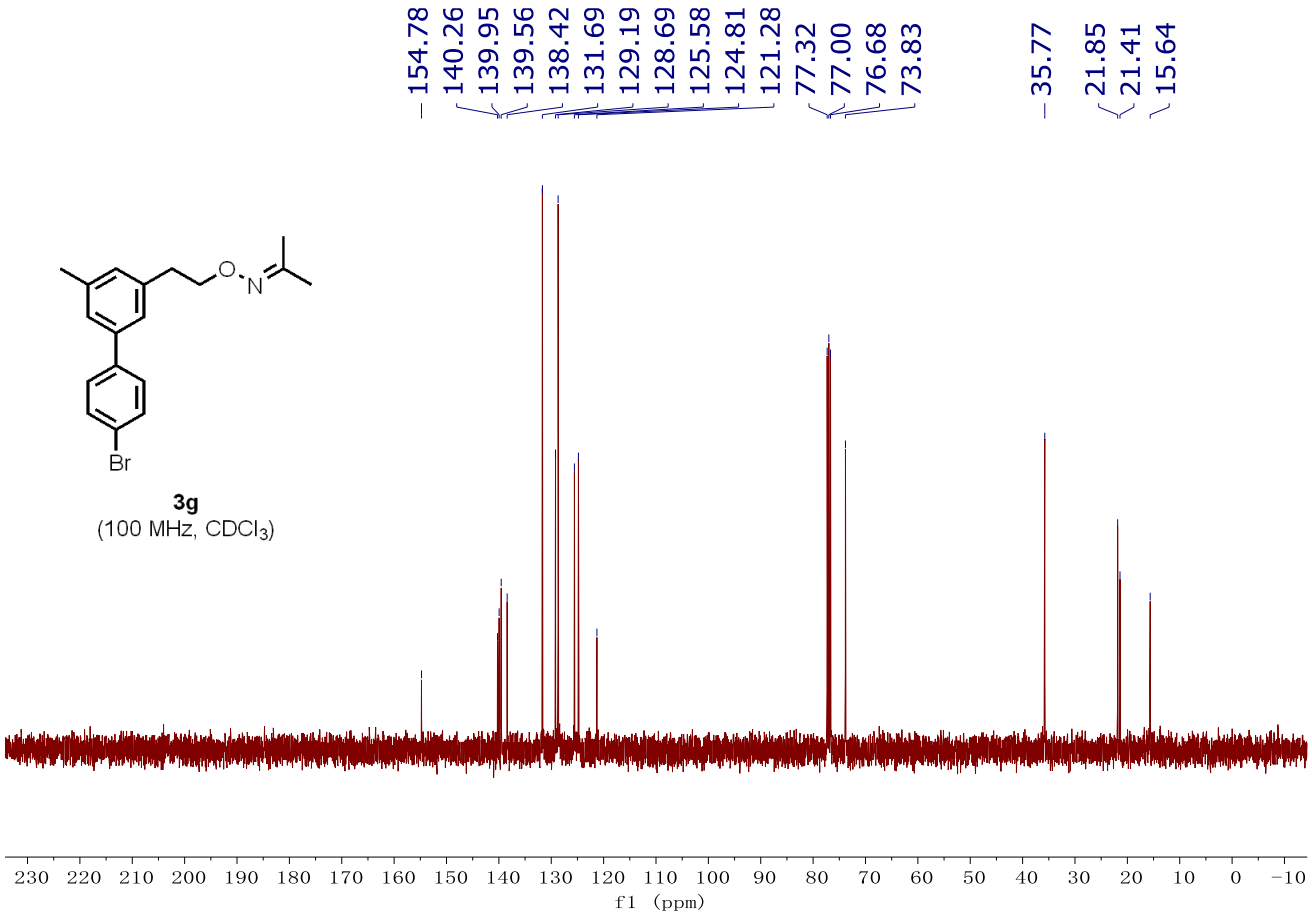

163.57
161.12
154.78
140.24
139.45
138.33
137.50
137.46
128.81
128.66
128.58
125.70
124.92
115.55
115.34
77.32
77.00
76.68
73.88
35.80
21.85
21.41
15.64
O
N
F
3e
(400 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

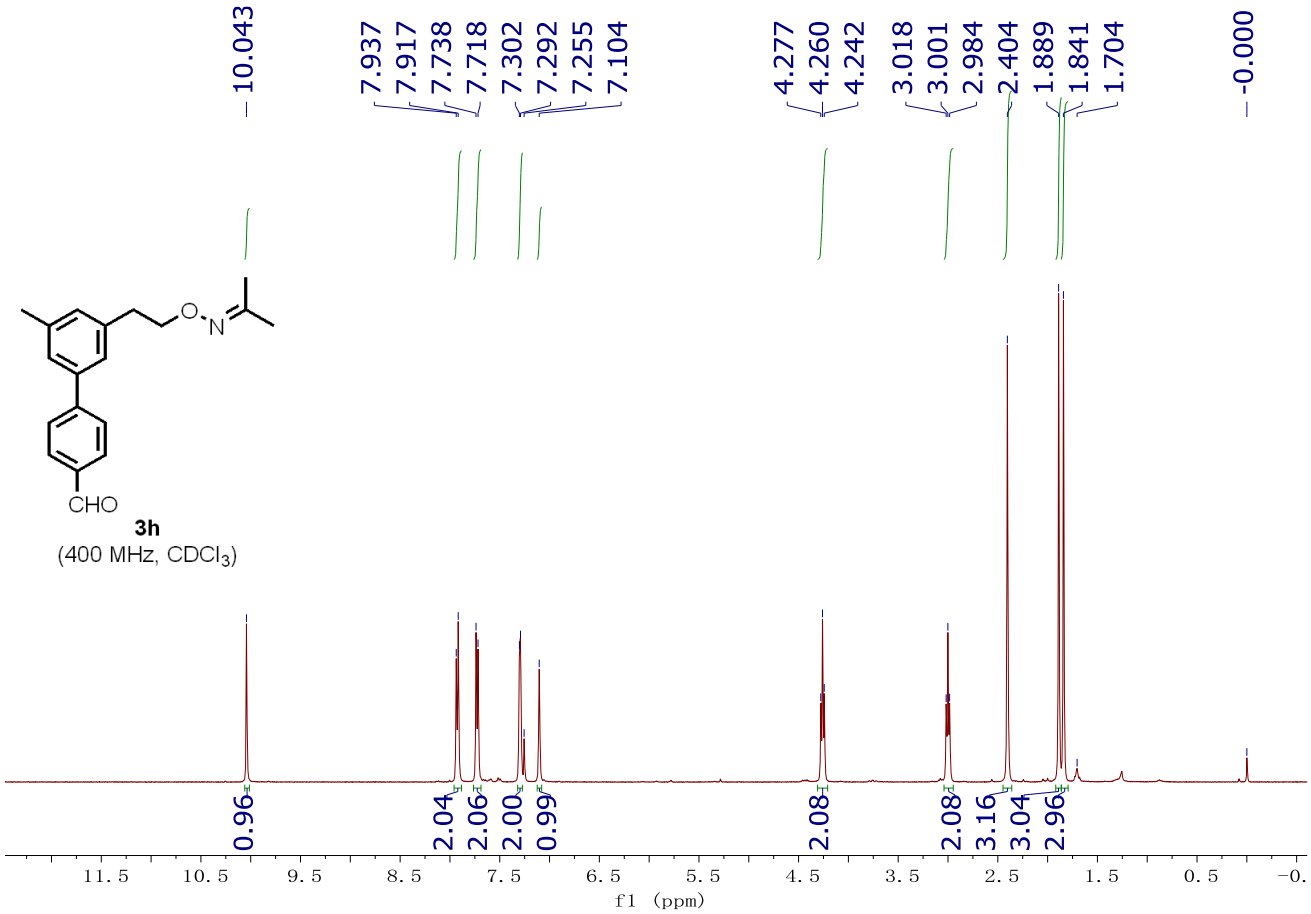

0.000
-116.577
-116.590
-116.595
-116.604
-116.626
O
N
F
3e
(375 MHz, CDCl3)
50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250
f1 (ppm)

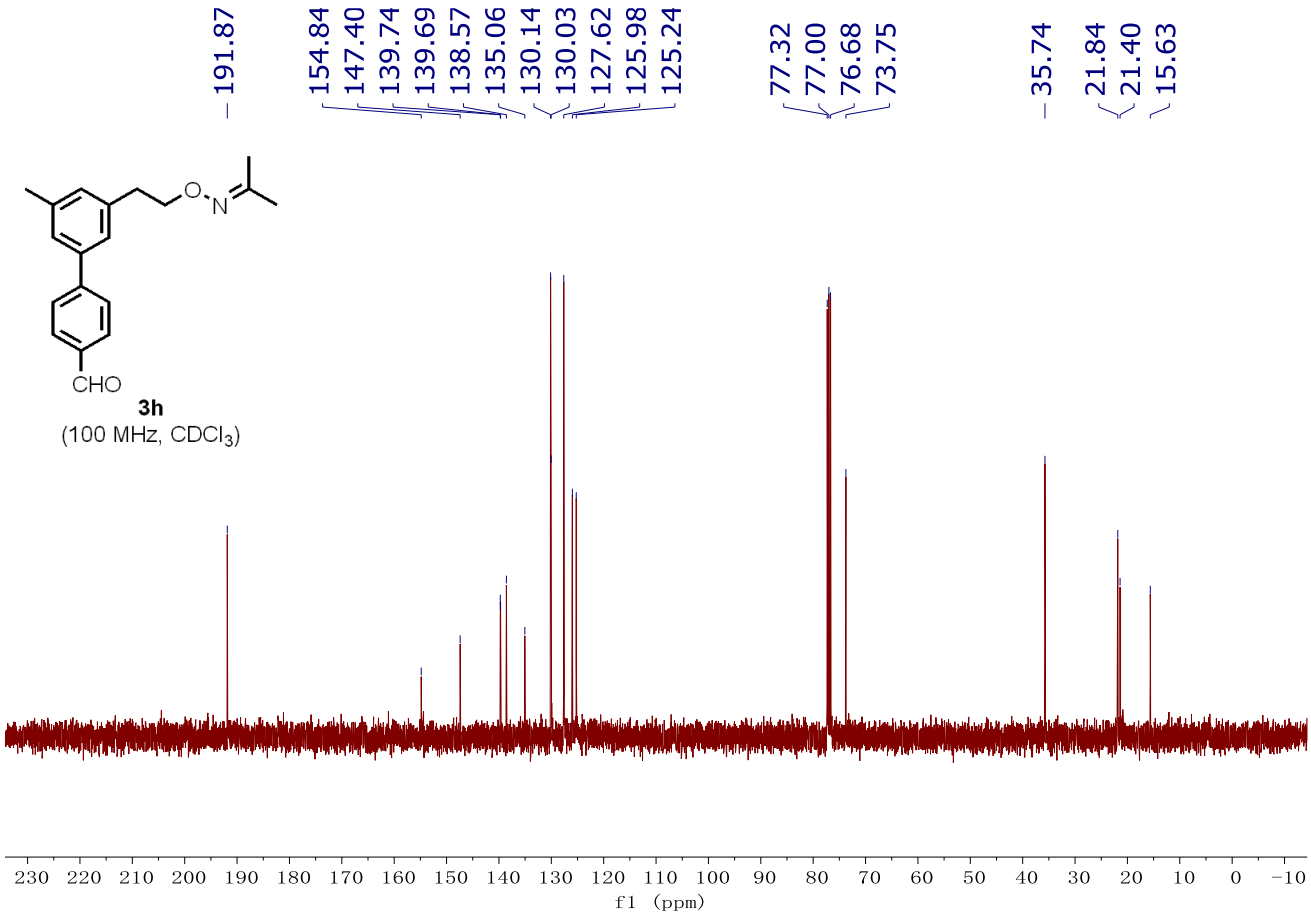

7.492
7.472
7.379
7.358
7.235
7.209
7.202
7.043
4.263
4.246
4.229
2.994
2.976
2.959
2.376
1.882
1.835
1.669
0.000
O
N
Cl
3f
(400 MHz, CDCl3)
2.00
1.88
1.01
0.92
1.04
2.15
2.15
3.16
2.90
2.85
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.
f1 (ppm)

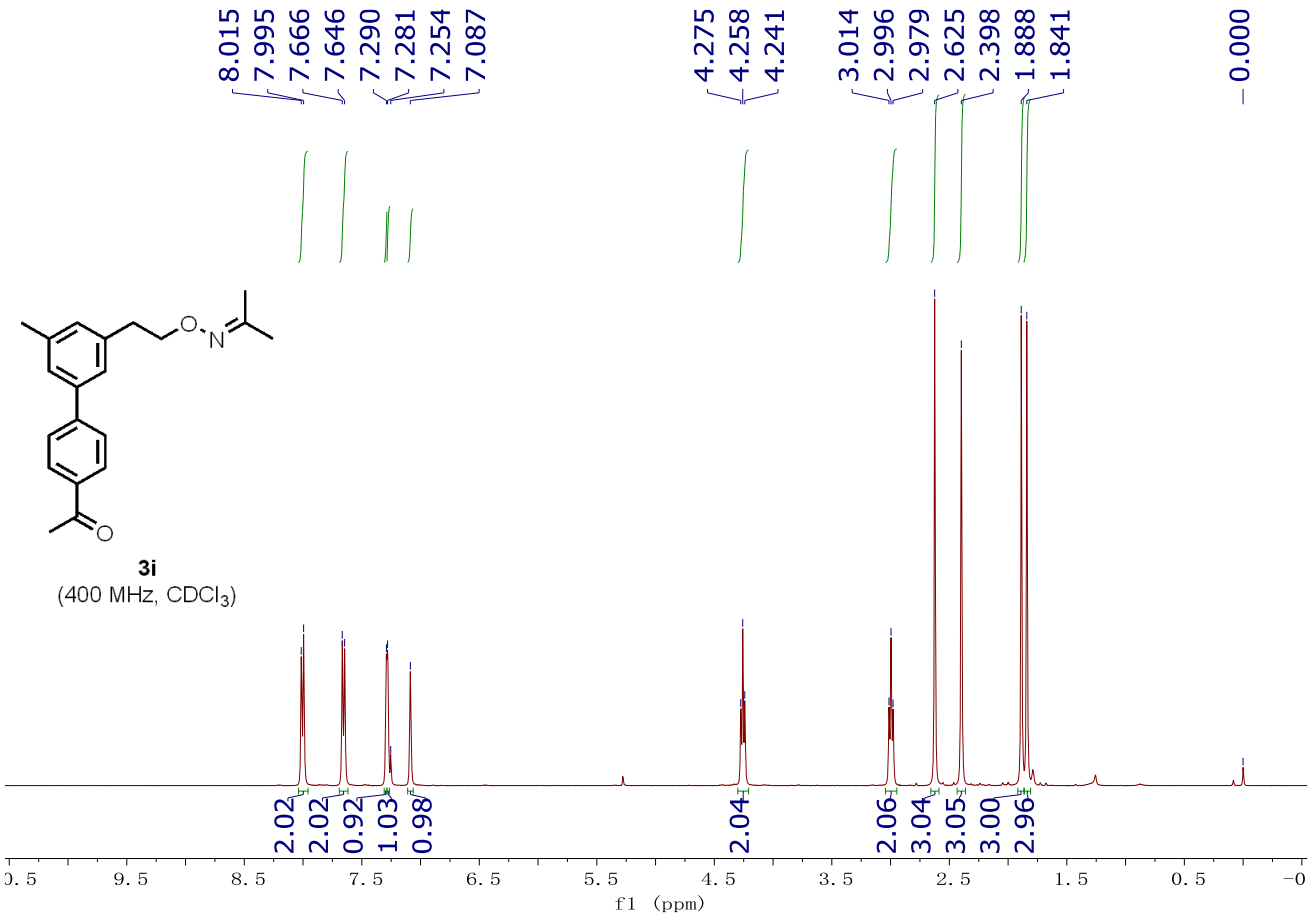

154.78
139.95
139.80
139.53
138.39
133.11
129.13
128.74
128.33
125.62
124.85
77.32
77.00
76.68
73.83
35.77
21.84
21.40
15.63
O
N
Cl
3f
(100 MHz, CDCl3)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−2
f1 (ppm)


7.536
7.515
7.431
7.410
7.237
7.207
7.200
7.046
4.262
4.244
4.227
2.994
2.976
2.959
2.377
1.883
1.835
1.648
-0.000
Br
3g
(400 MHz, CDCl3)
1.96
2.05
0.92
1.05
0.98
2.08
2.09
3.09
3.00
2.94
f1 (ppm)

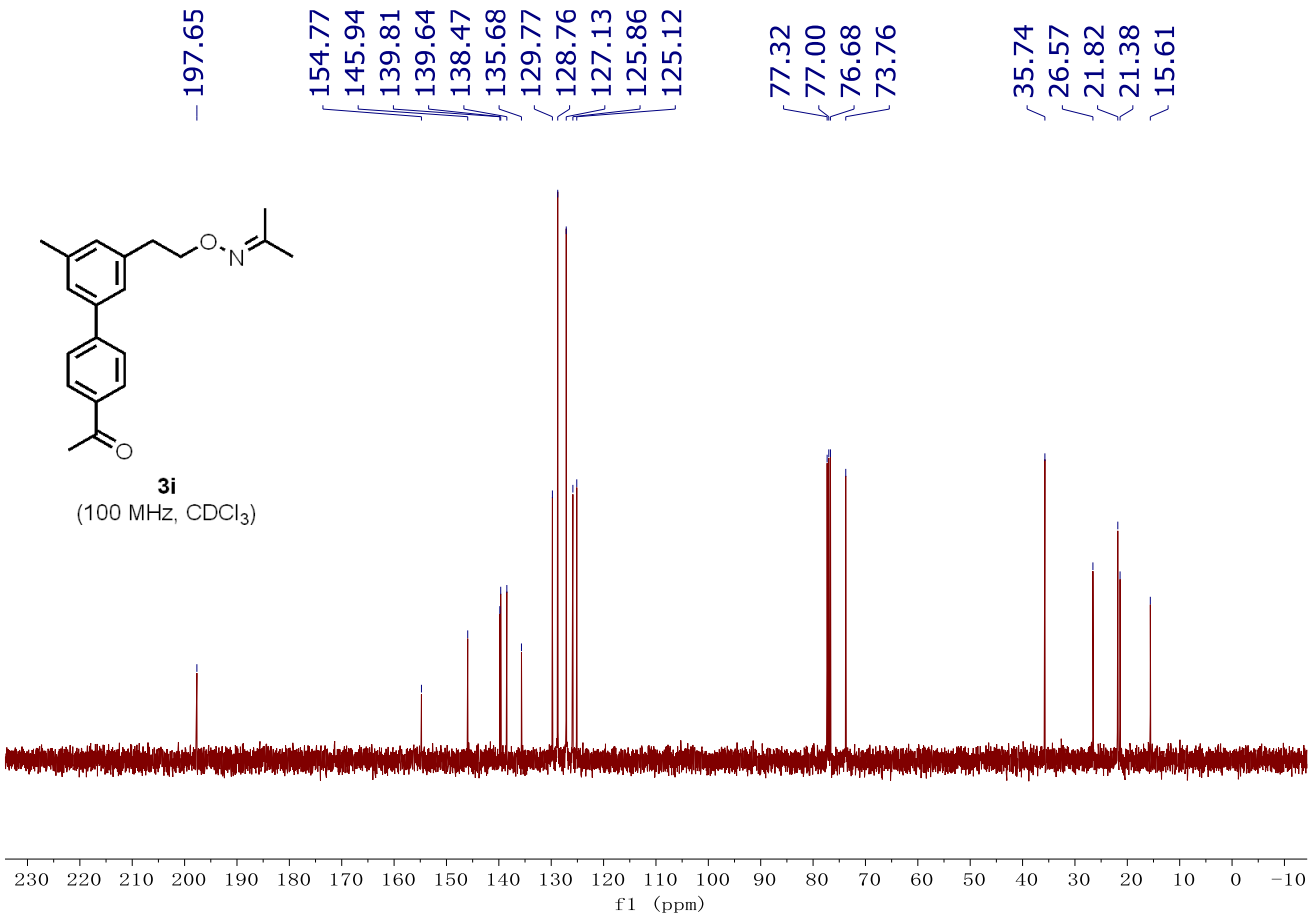

154.78
140.26
139.95
139.56
138.42
131.69
129.19
128.69
125.58
124.81
121.28
77.32
77.00
76.68
73.83
35.77
21.85
21.41
15.64
Br
3g
(100 MHz, CDCl3)
f1 (ppm)


10.043
7.937
7.917
7.738
7.718
7.302
7.292
7.255
7.104
4.277
4.260
4.242
3.018
3.001
2.984
2.404
1.889
1.841
1.704
-0.000
0.96
2.04
2.06
2.00
0.99
2.08
2.08
3.16
3.04
2.96
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)
CHO
3h
(400 MHz, CDCl3)

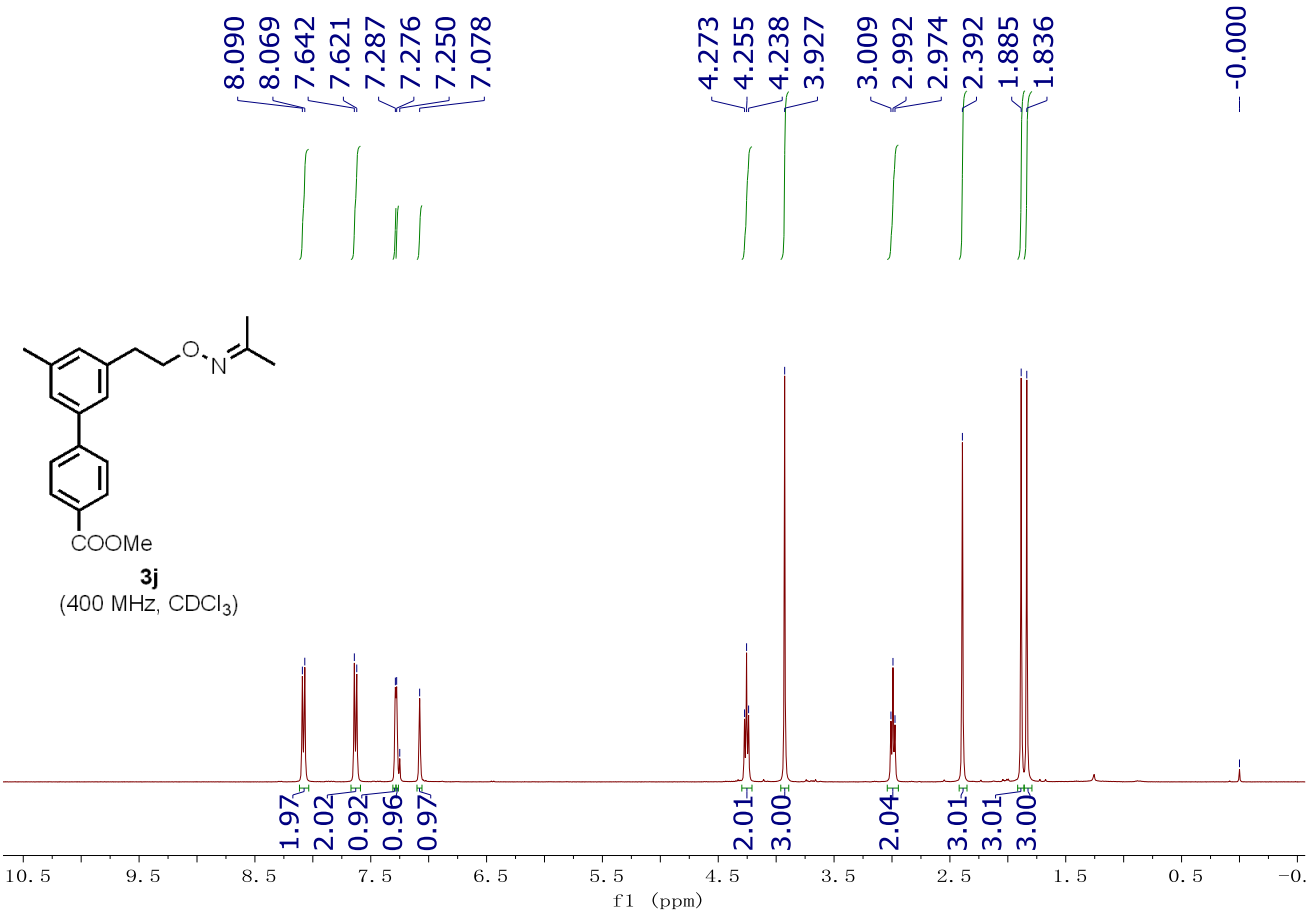

191.87
154.84
147.40
139.74
139.69
138.57
135.06
130.14
130.03
127.62
125.98
125.24
77.32
77.00
76.68
73.75
35.74
21.84
21.40
15.63
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
CHO
3h
(100 MHz, CDCl3)

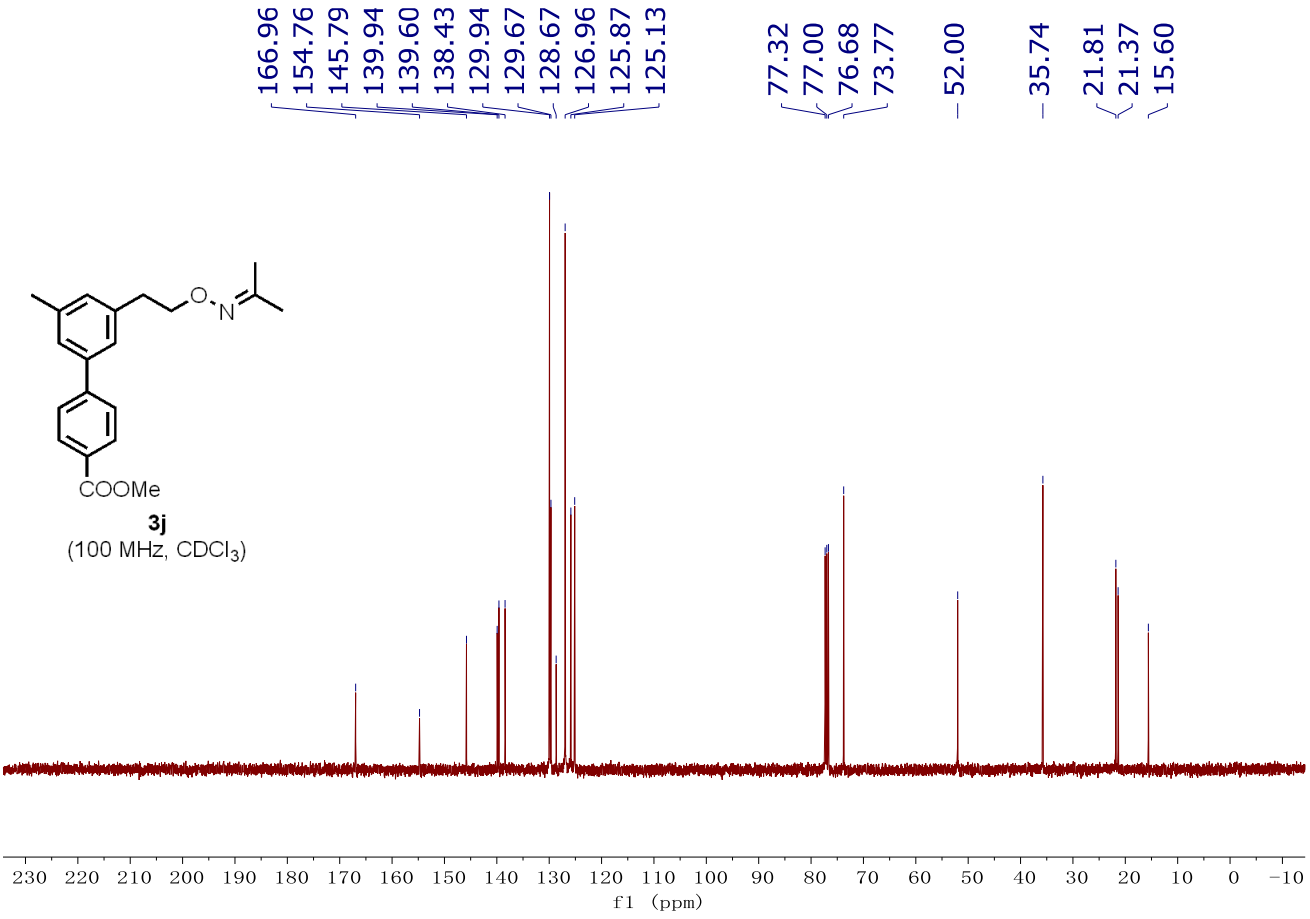


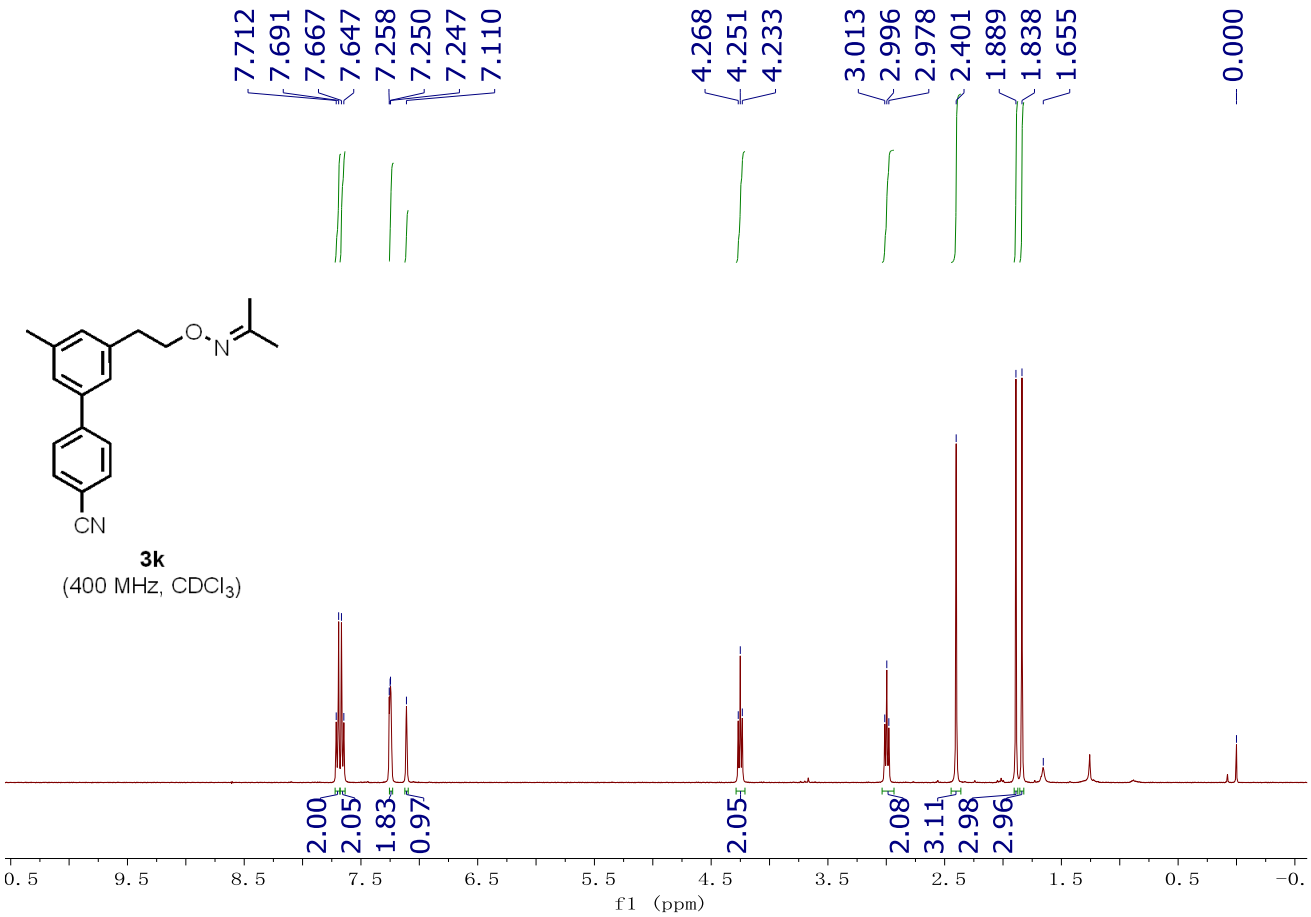
3i
(400 MHz, $CDCl_3$)

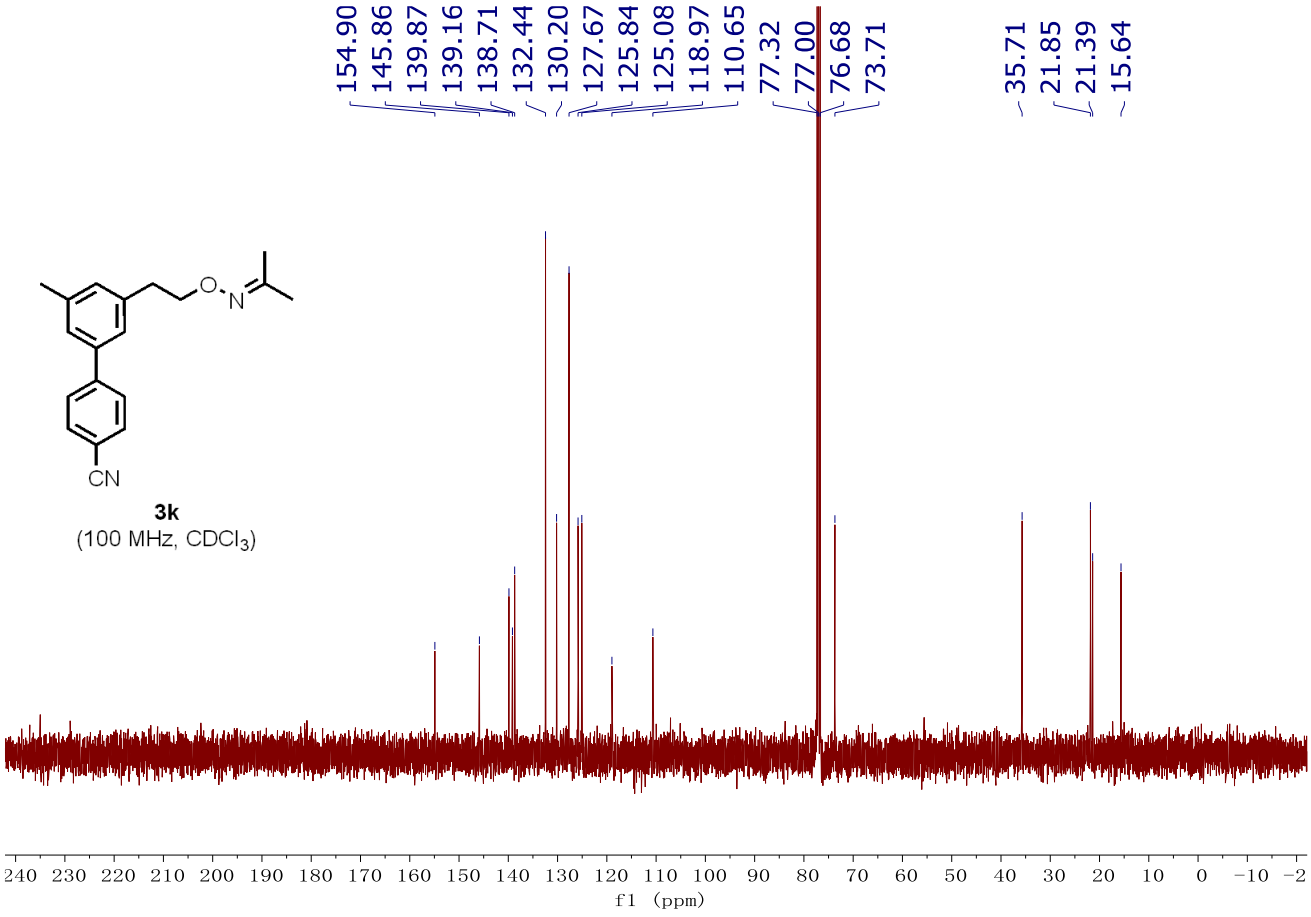


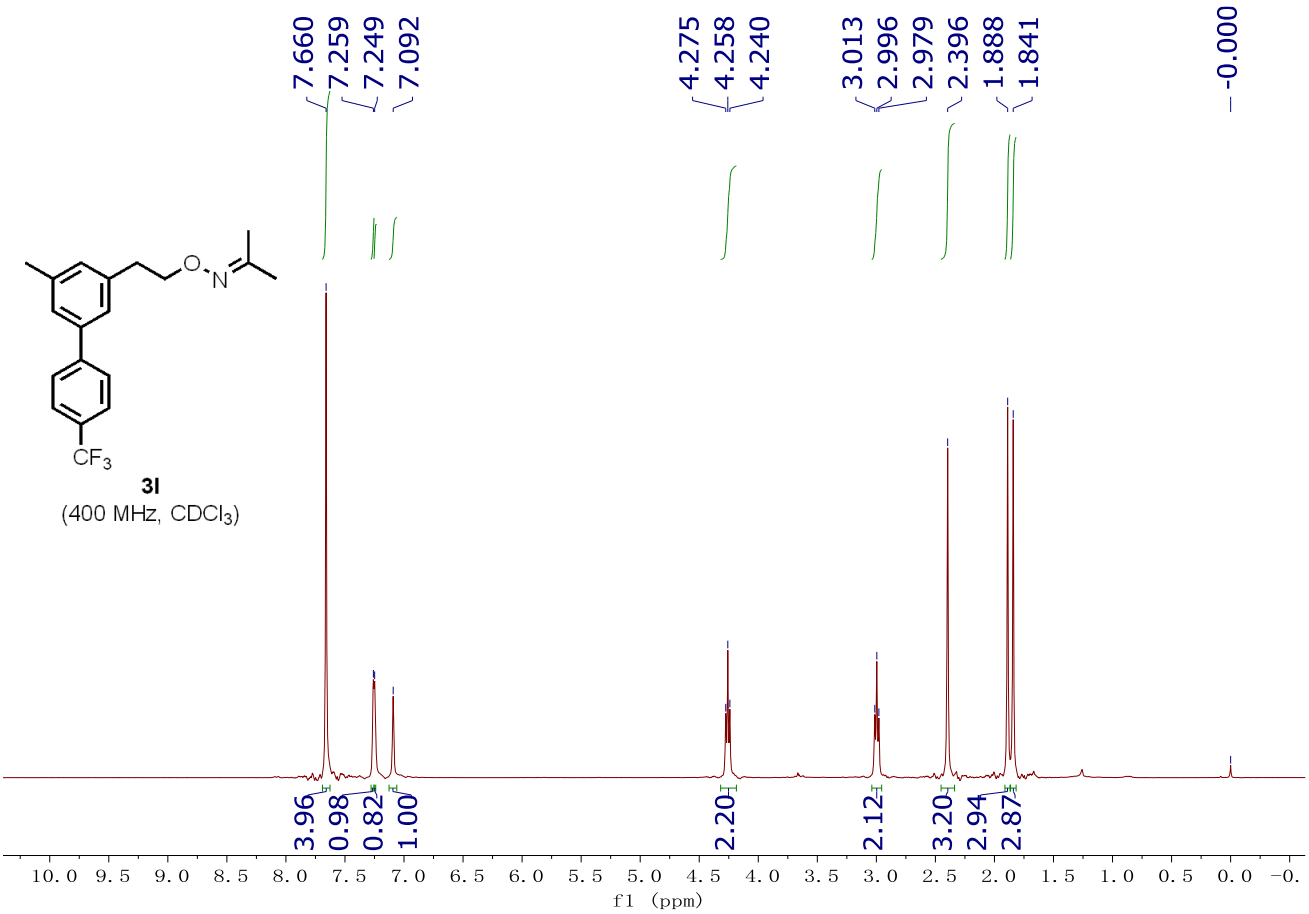
3i
(100 MHz, $CDCl_3$)


8.090
8.069
7.642
7.621
7.287
7.276
7.250
7.078
4.273
4.255
4.238
3.927
3.009
2.992
2.974
2.392
1.885
1.836
-0.000
COOMe
3j
(400 MHz, CDCl3)
1.97
2.02
0.92
0.96
0.97
2.01
3.00
2.04
3.01
3.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)

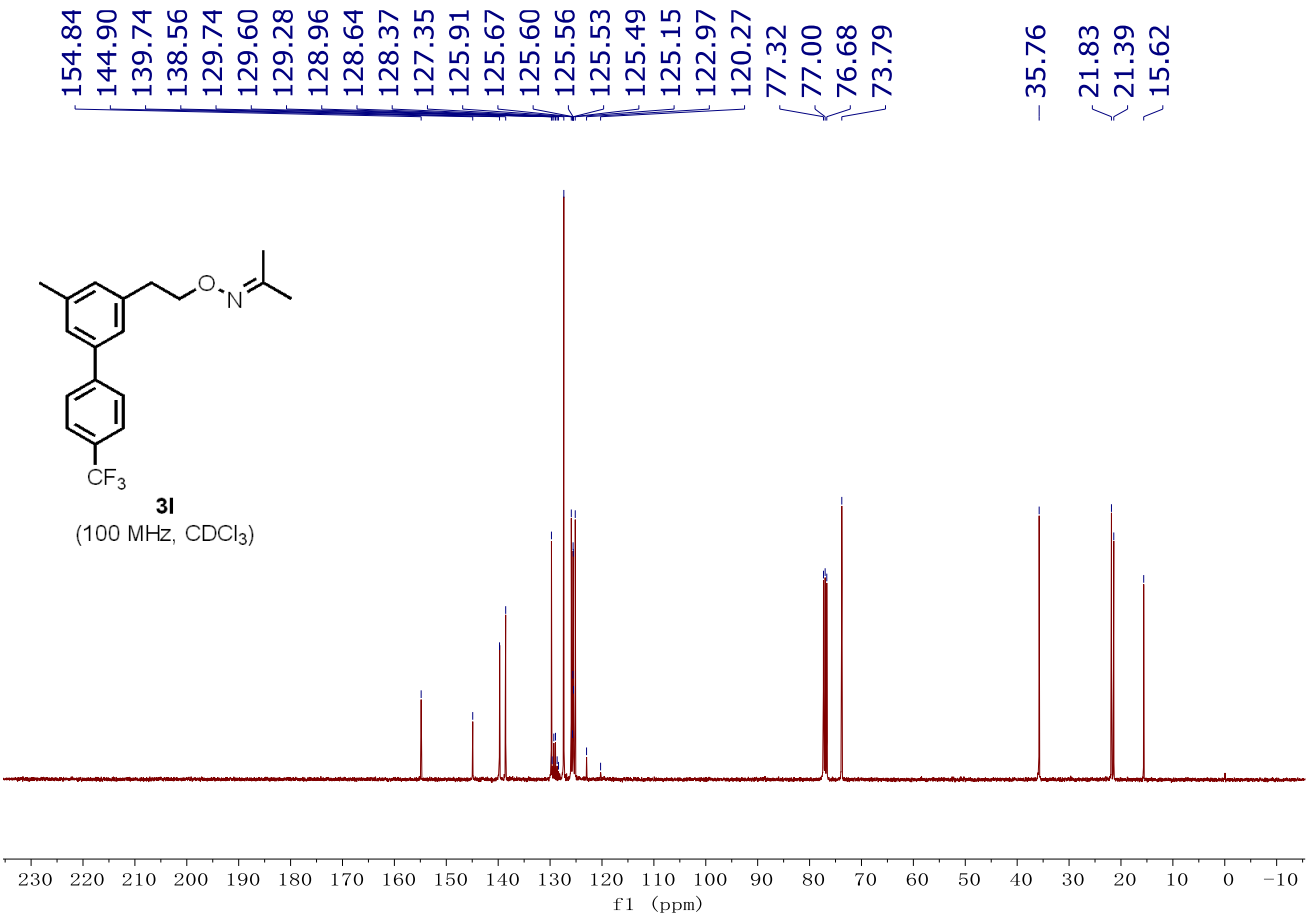

166.96
154.76
145.79
139.94
139.60
138.43
129.94
129.67
128.67
126.96
125.87
125.13
77.32
77.00
76.68
73.77
52.00
35.74
21.81
21.37
15.60
COOMe
3j
(100 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.712
7.691
7.667
7.647
7.258
7.250
7.247
7.110
4.268
4.251
4.233
3.013
2.996
2.978
2.401
1.889
1.838
1.655
0.000
O
N
CN
3k
(400 MHz, CDCl3)
2.00
2.05
1.83
0.97
2.05
2.08
3.11
2.98
2.96
f1 (ppm)

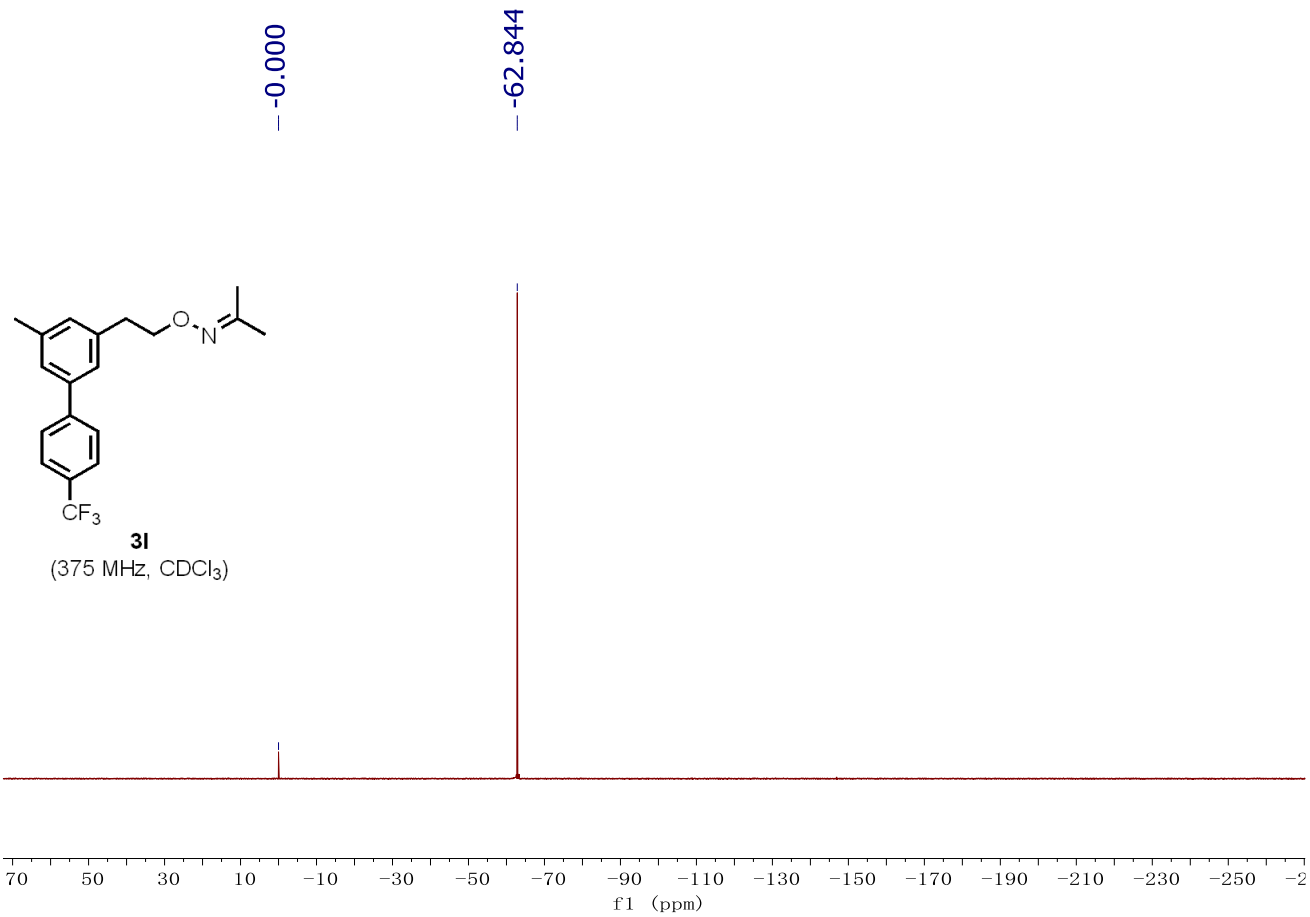

154.90
145.86
139.87
139.16
138.71
132.44
130.20
127.67
125.84
125.08
118.97
110.65
77.32
77.00
76.68
73.71
35.71
21.85
21.39
15.64
O
N
CN
3k
(100 MHz, CDCl3)
f1 (ppm)



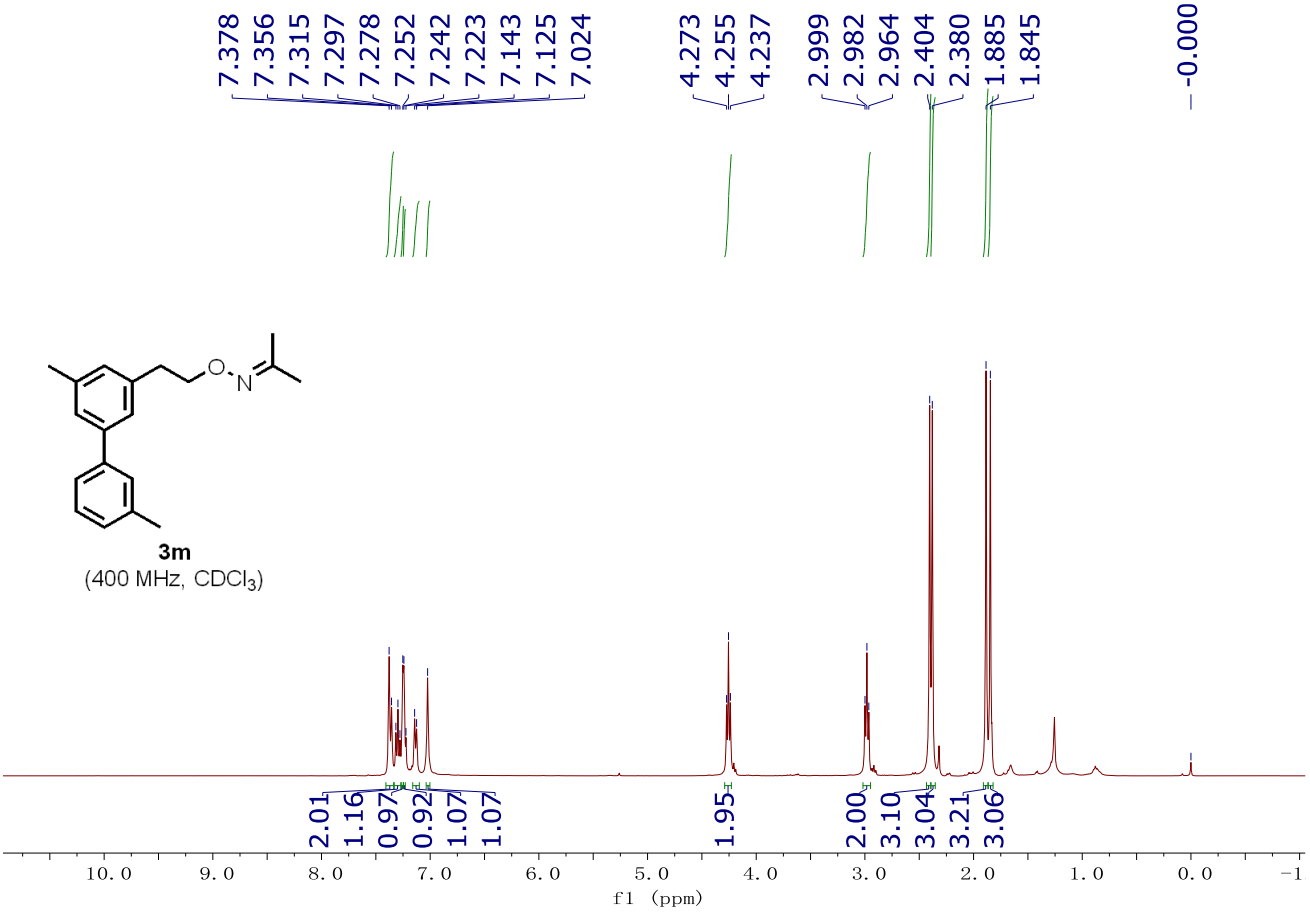
3l
(400 MHz, $CDCl_3$)



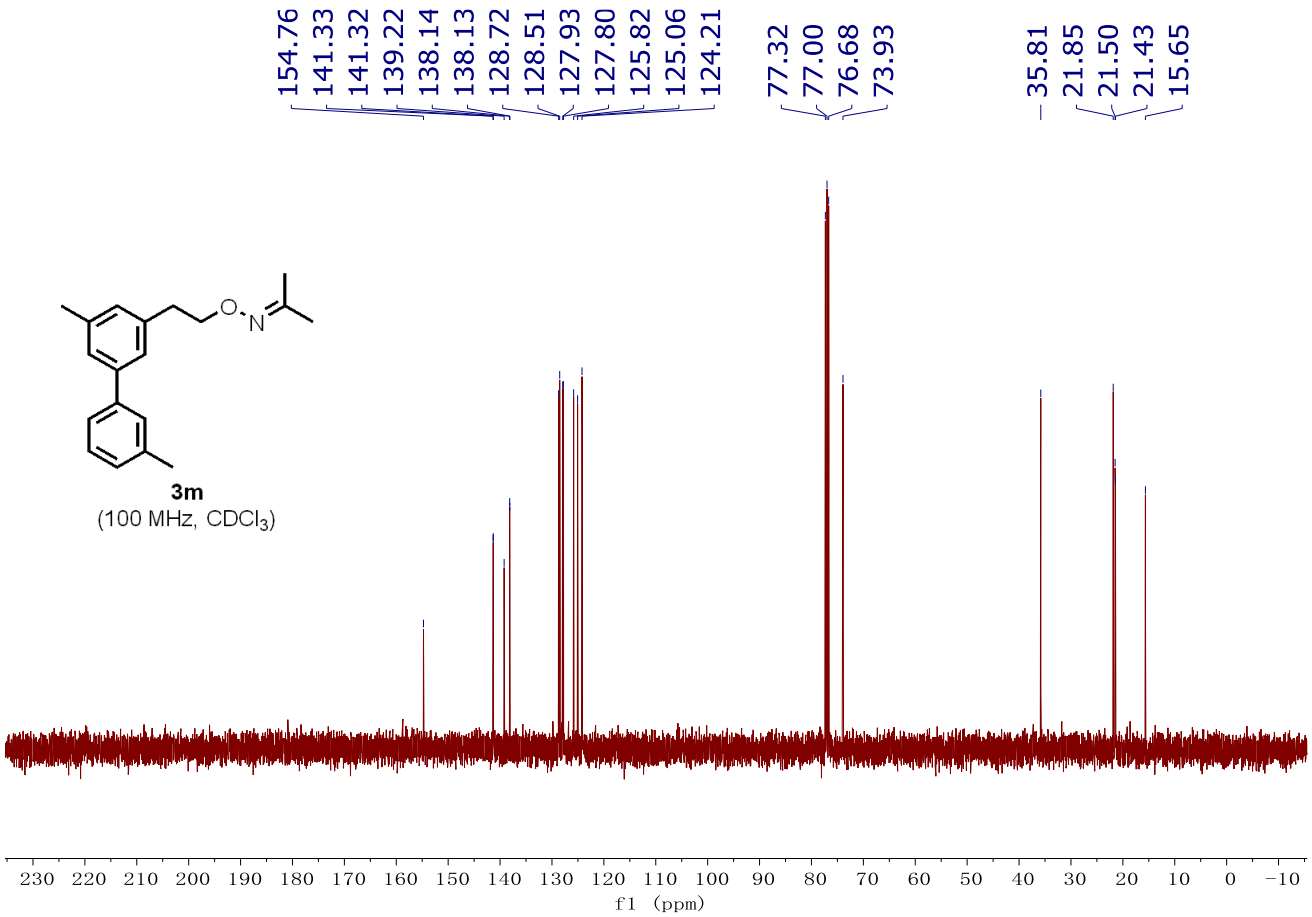
3l
(100 MHz, $CDCl_3$)

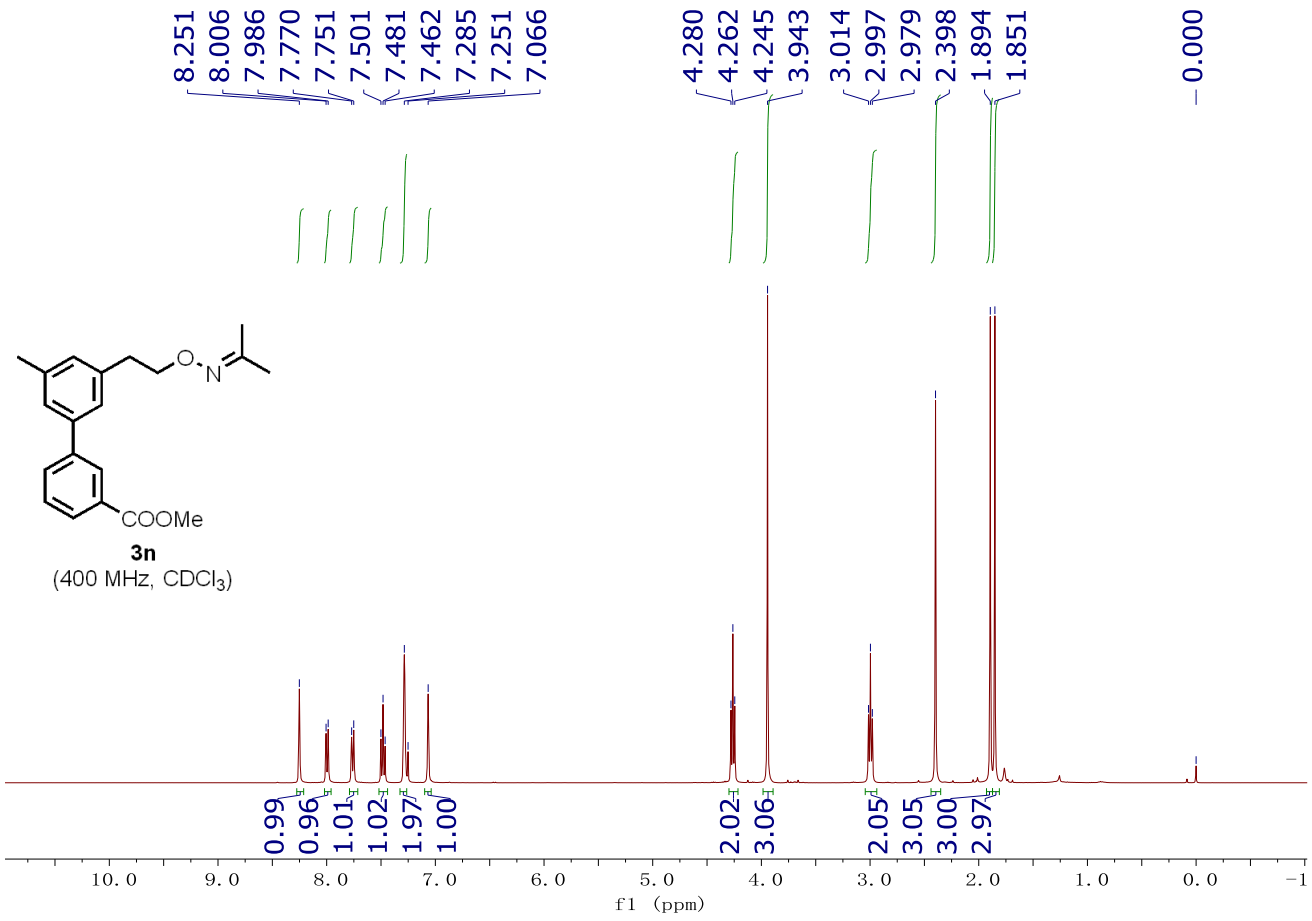


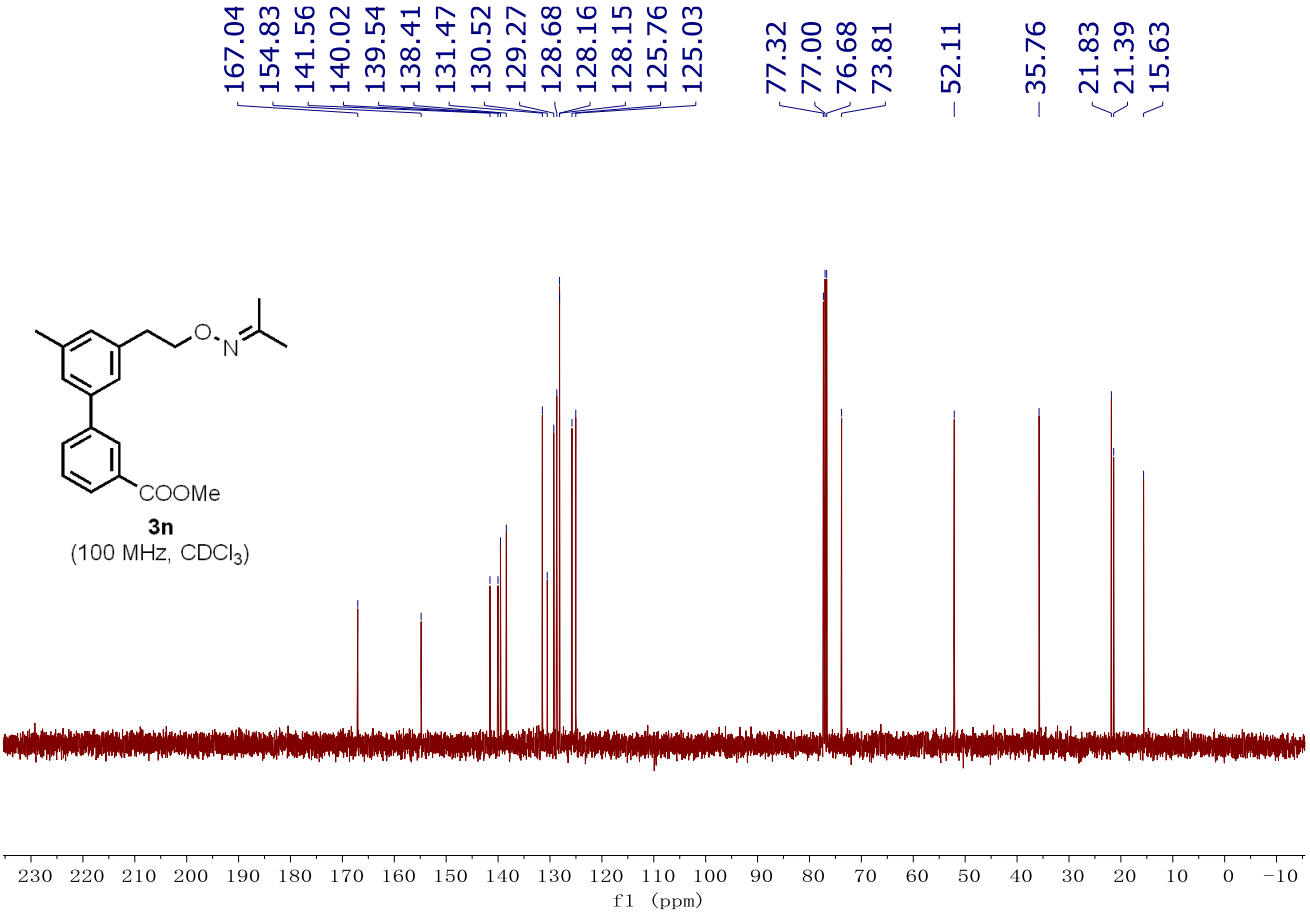
3l
(375 MHz, $CDCl_3$)

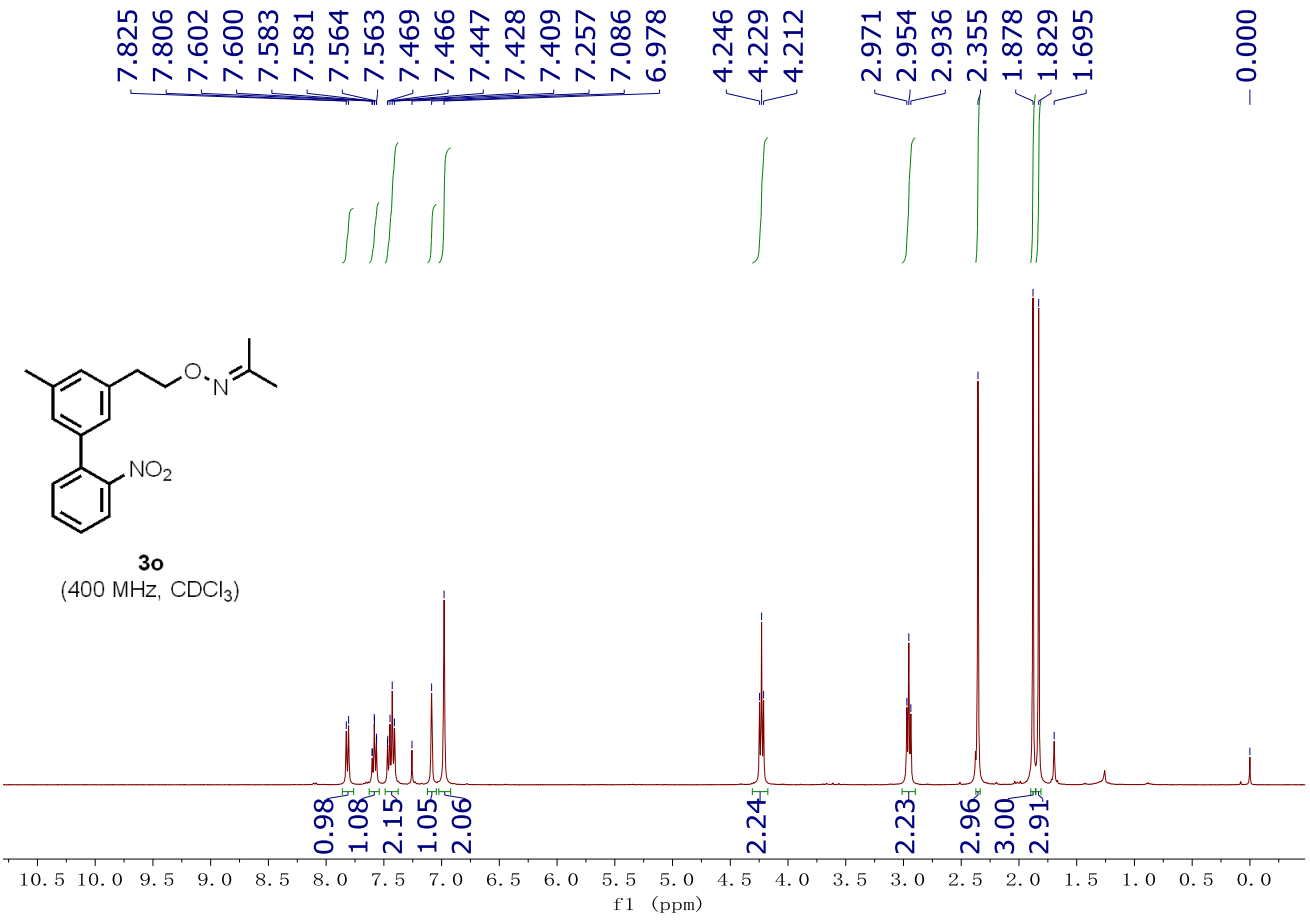


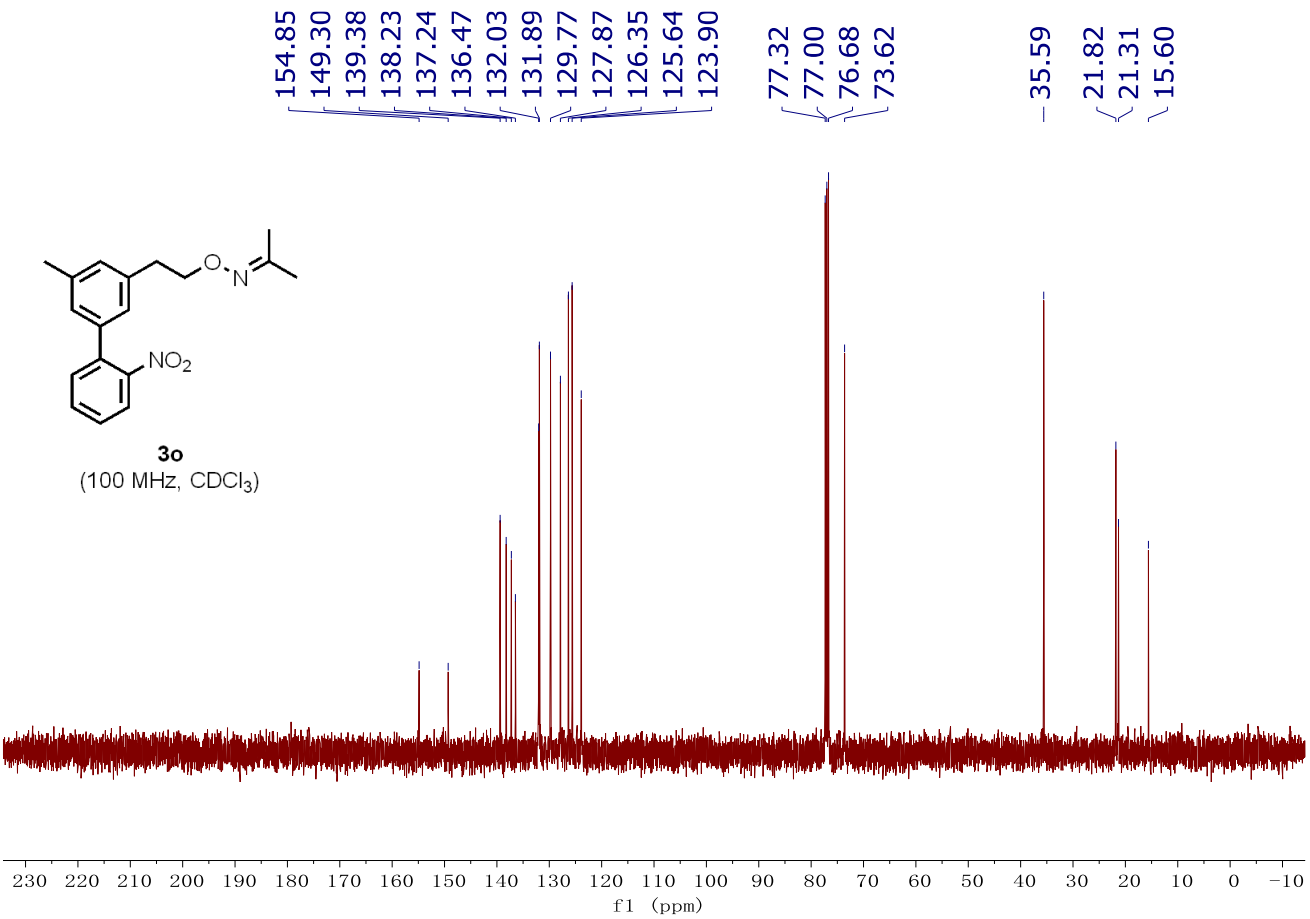
3m
(400 MHz, $CDCl_3$)

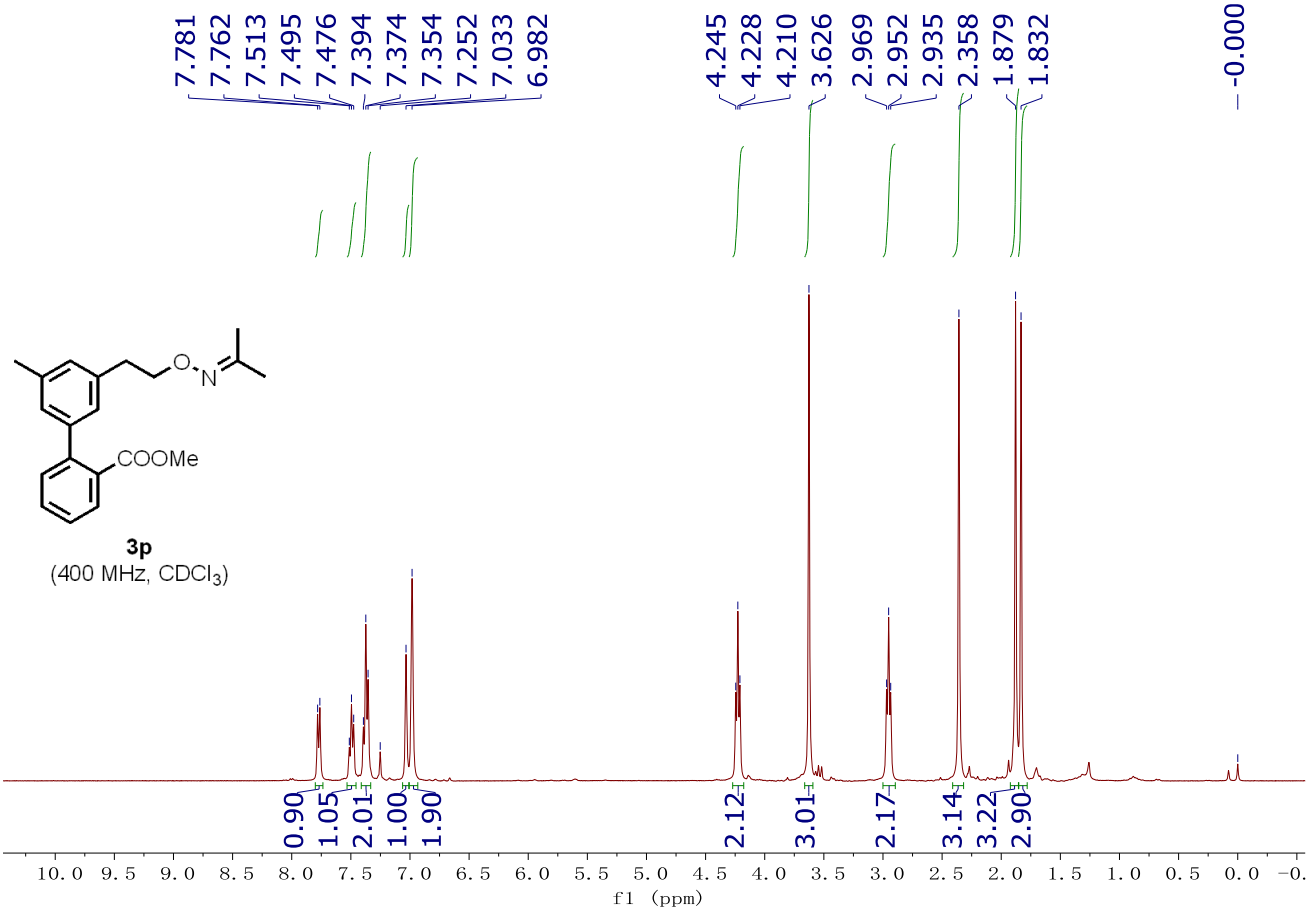

154.76
141.33
141.32
139.22
138.14
138.13
128.72
128.51
127.93
127.80
125.82
125.06
124.21
77.32
77.00
76.68
73.93
35.81
21.85
21.50
21.43
15.65
O
N
3m
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

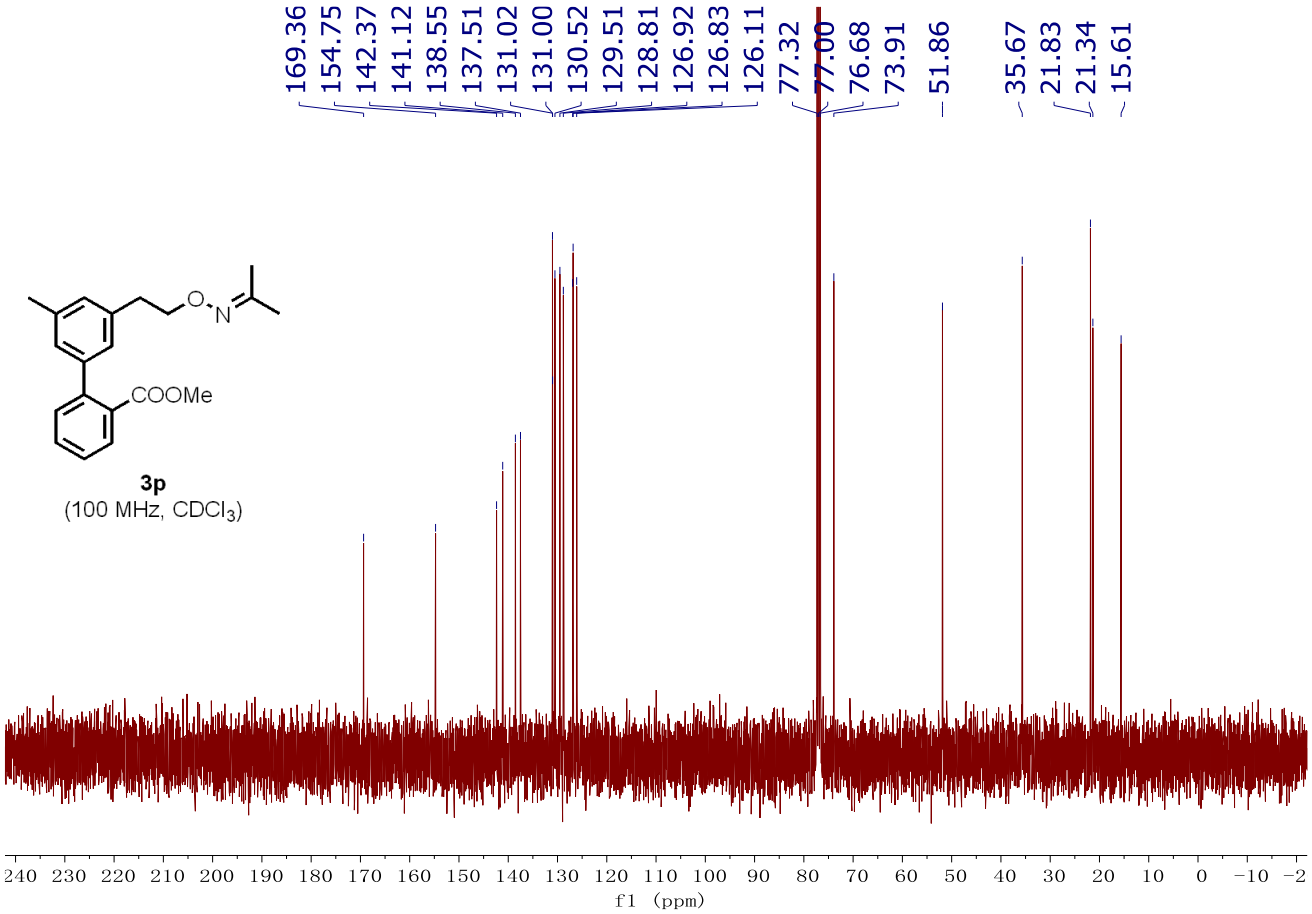

8.251
8.006
7.986
7.770
7.751
7.501
7.481
7.462
7.285
7.251
7.066
4.280
4.262
4.245
3.943
3.014
2.997
2.979
2.398
1.894
1.851
0.000
O
N
COOMe
3n
(400 MHz, CDCl3)
0.99
0.96
1.01
1.02
1.97
1.00
2.02
3.06
2.05
3.05
3.00
2.97
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1
f1 (ppm)

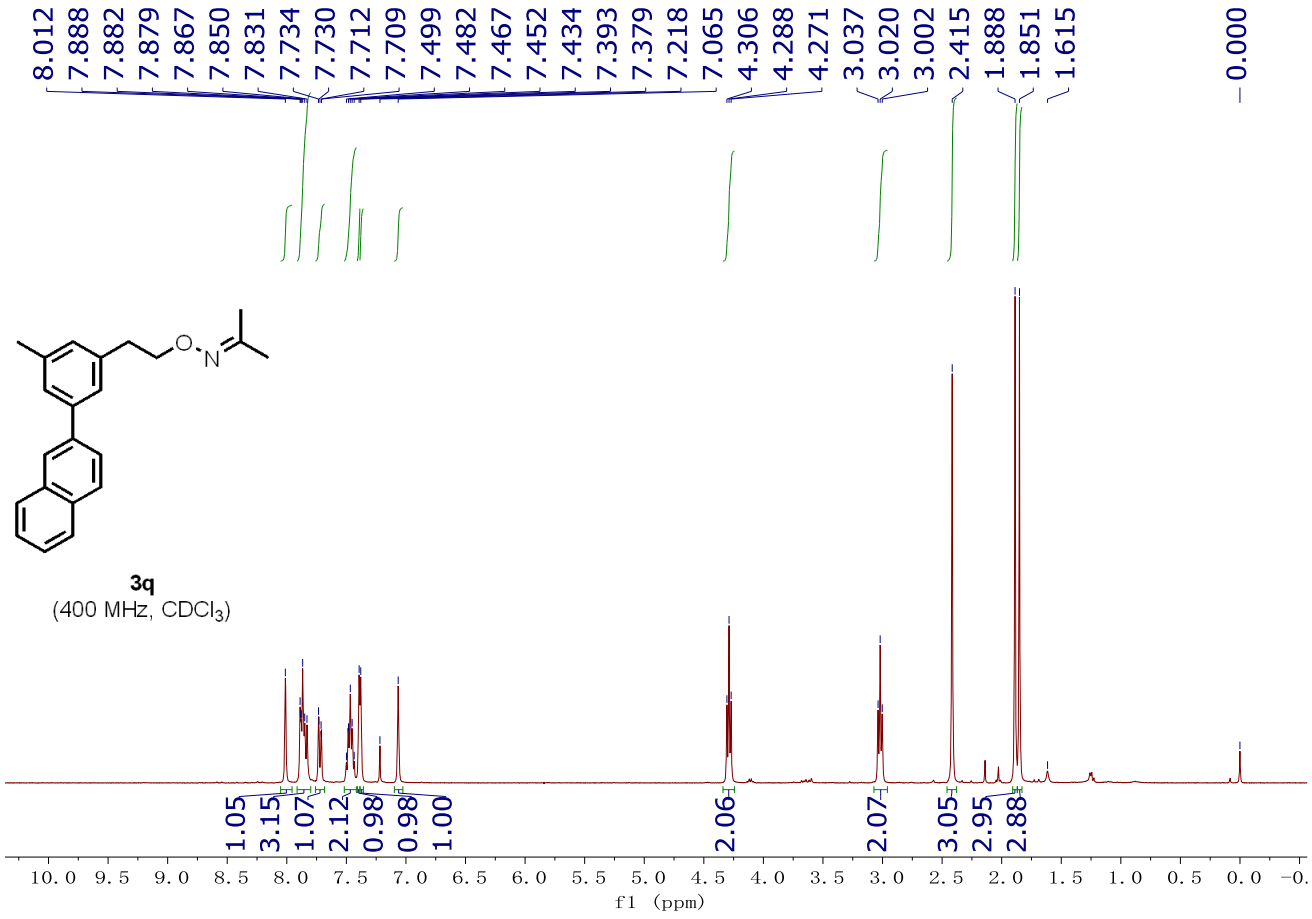

167.04
154.83
141.56
140.02
139.54
138.41
131.47
130.52
129.27
128.68
128.16
128.15
125.76
125.03
77.32
77.00
76.68
73.81
52.11
35.76
21.83
21.39
15.63
O
N
COOMe
3n
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

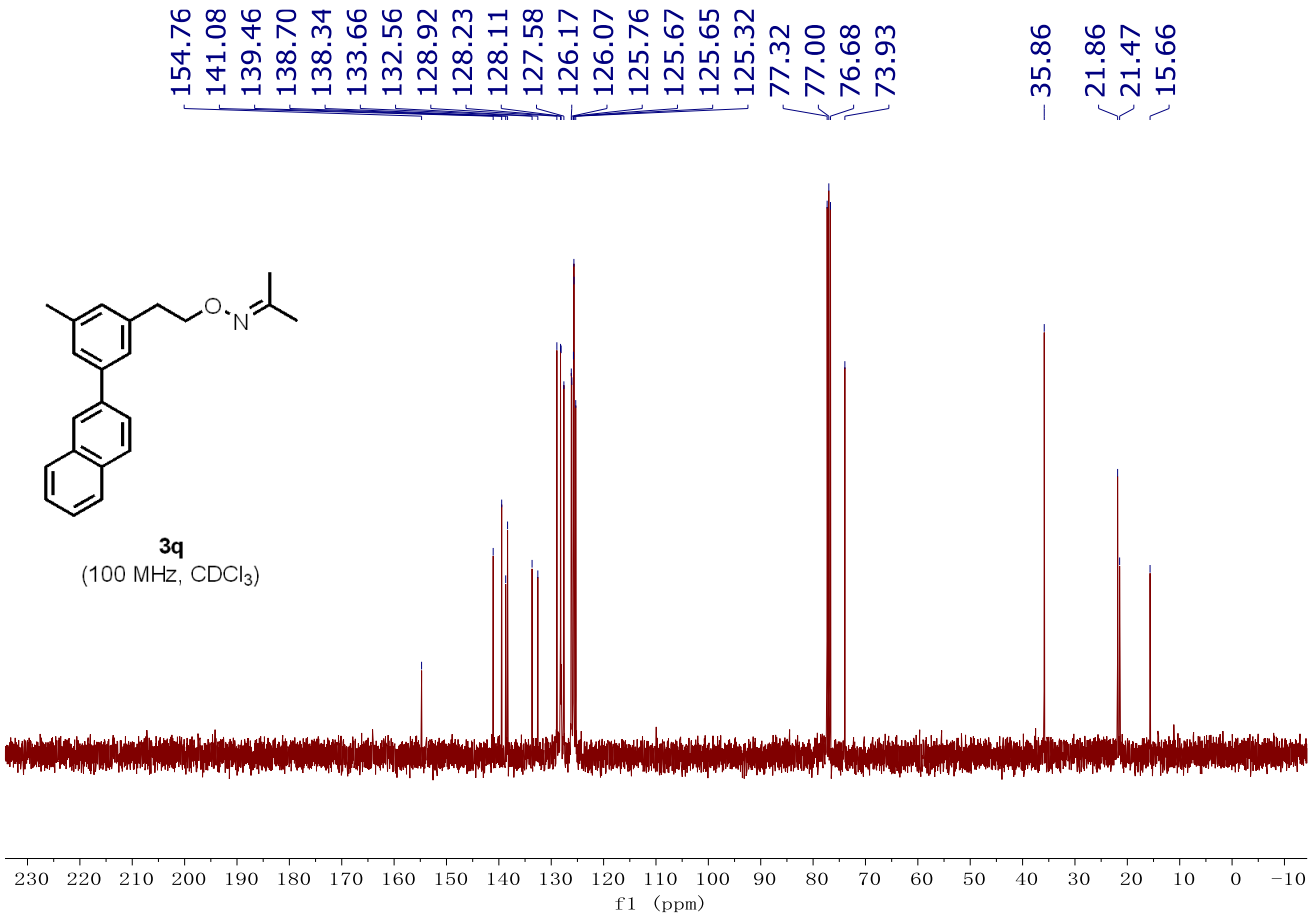

7.825
7.806
7.602
7.600
7.583
7.581
7.564
7.563
7.469
7.466
7.447
7.428
7.409
7.257
7.086
6.978
4.246
4.229
4.212
2.971
2.954
2.936
2.355
1.878
1.829
1.695
0.000
O
N
NO2
3o
(400 MHz, CDCl3)
0.98
1.08
2.15
1.05
2.06
2.24
2.23
2.96
3.00
2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

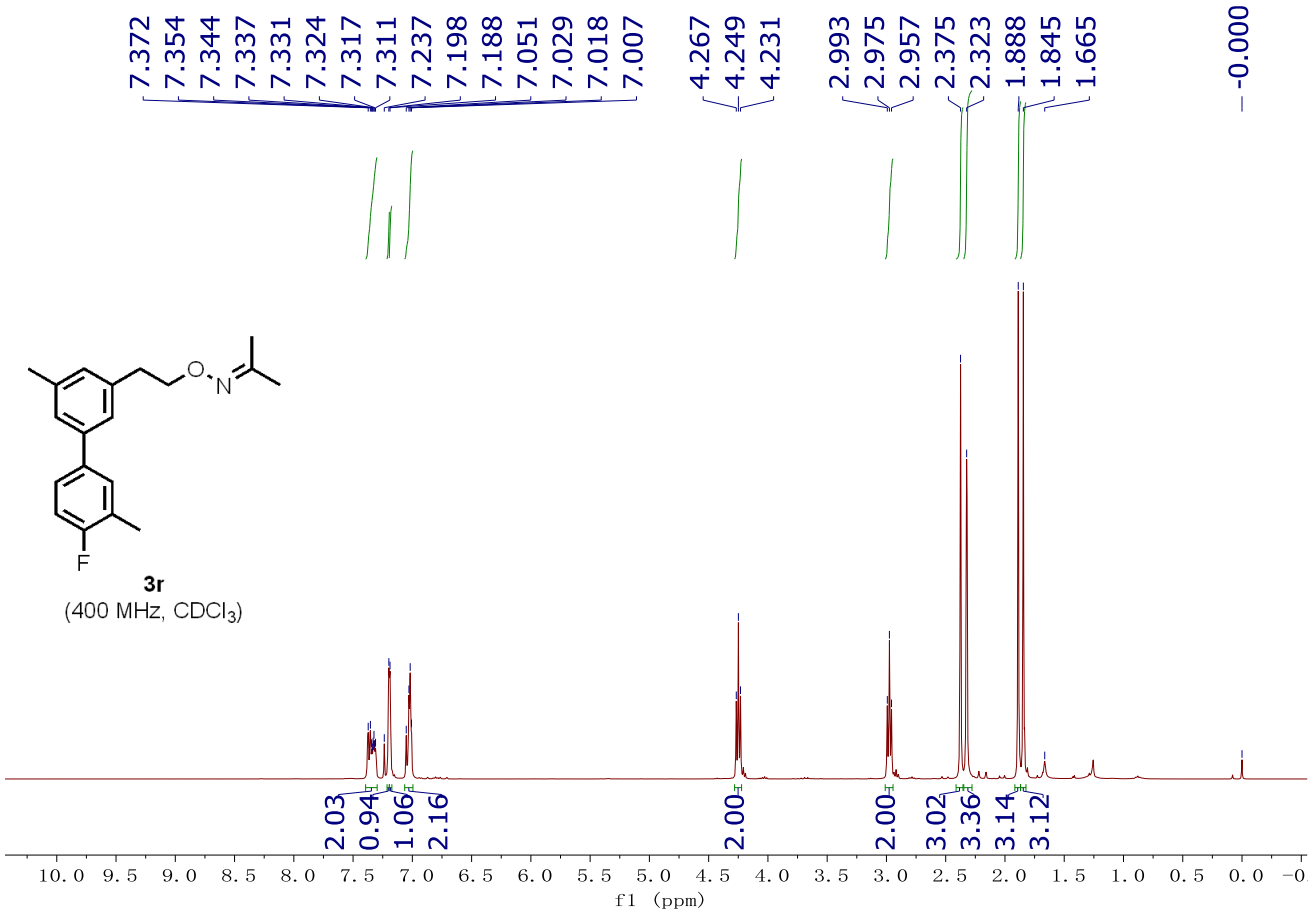

154.85
149.30
139.38
138.23
137.24
136.47
132.03
131.89
129.77
127.87
126.35
125.64
123.90
77.32
77.00
76.68
73.62
35.59
21.82
21.31
15.60
NO2
3o
(100 MHz, CDCl3)
f1 (ppm)

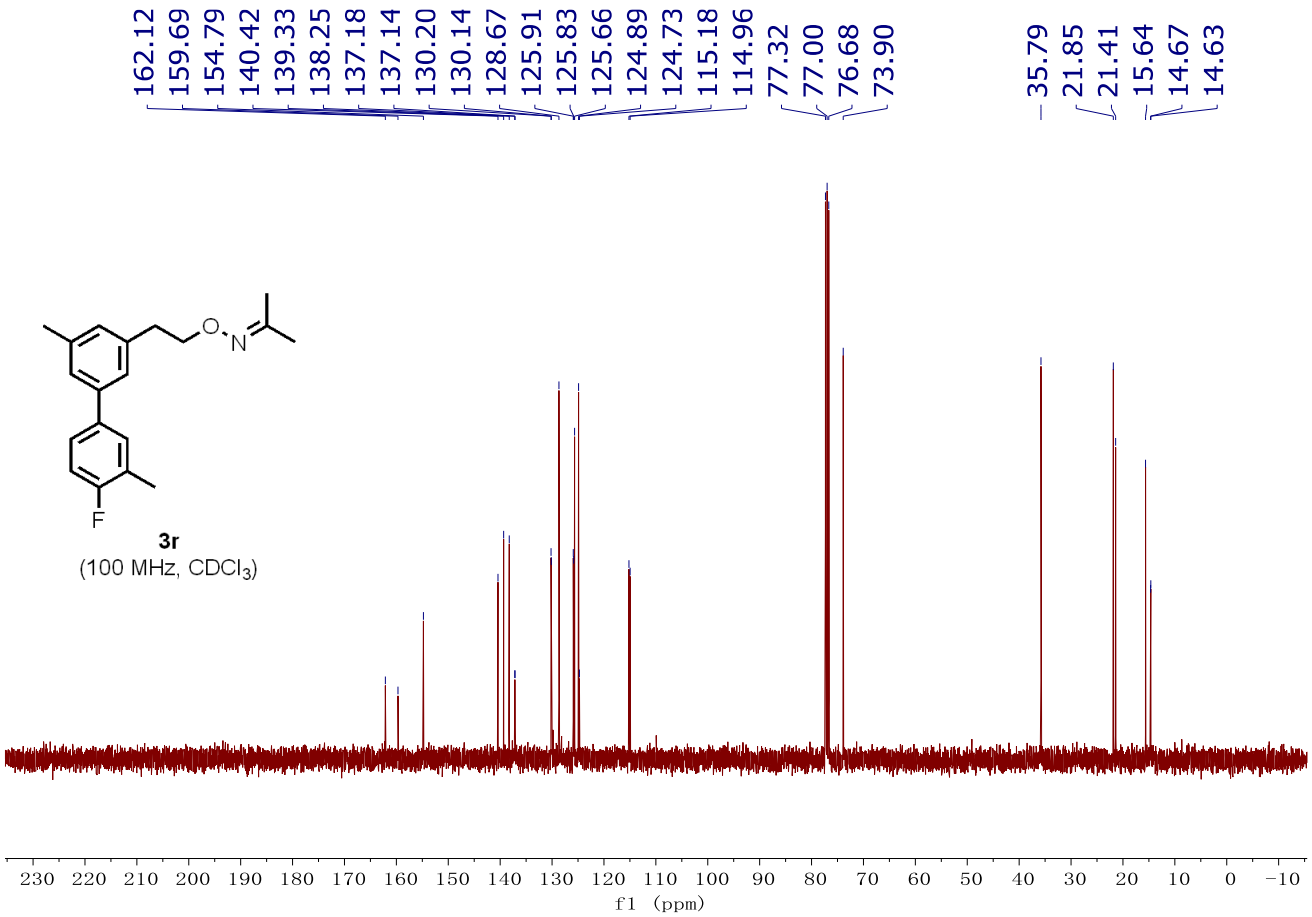

7.781
7.762
7.513
7.495
7.476
7.394
7.374
7.354
7.252
7.033
6.982
4.245
4.228
4.210
3.626
2.969
2.952
2.935
2.358
1.879
1.832
-0.000
COOMe
3p
(400 MHz, CDCl3)
0.90
1.05
2.01
1.00
1.90
2.12
3.01
2.17
3.14
3.22
2.90
f1 (ppm)

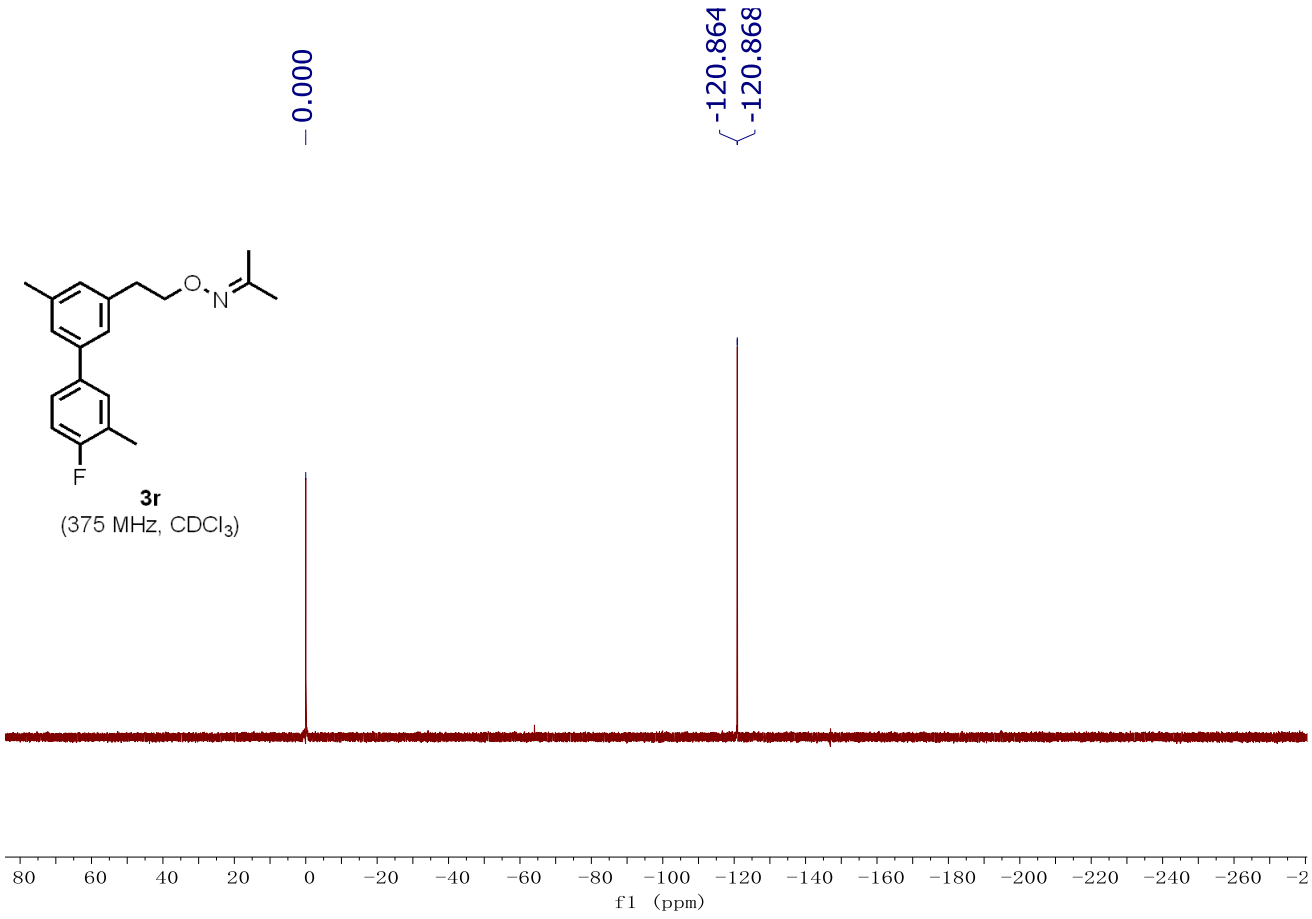

169.36
154.75
142.37
141.12
138.55
137.51
131.02
131.00
130.52
129.51
128.81
126.92
126.83
126.11
77.32
77.00
76.68
73.91
51.86
35.67
21.83
21.34
15.61
COOMe
3p
(100 MHz, CDCl3)
f1 (ppm)

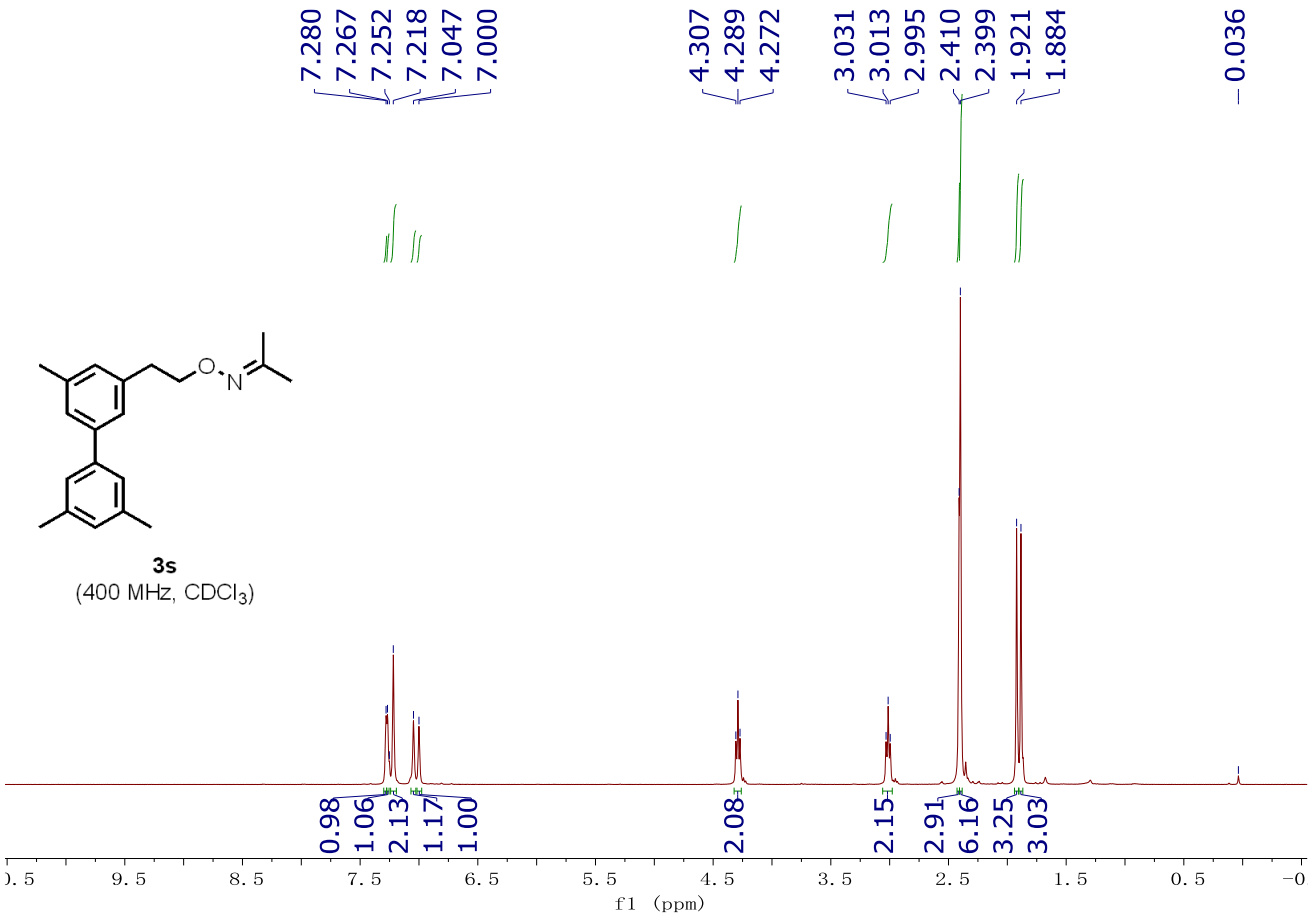

8.012
7.888
7.882
7.879
7.867
7.850
7.831
7.734
7.730
7.712
7.709
7.499
7.482
7.467
7.452
7.434
7.393
7.379
7.218
7.065
4.306
4.288
4.271
3.037
3.020
3.002
2.415
1.888
1.851
1.615
0.000
1.05
3.15
1.07
2.12
0.98
0.98
1.00
2.06
2.07
3.05
2.95
2.88
3q
(400 MHz, CDCl3)
f1 (ppm)


154.76
141.08
139.46
138.70
138.34
133.66
132.56
128.92
128.23
128.11
127.58
126.17
126.07
125.76
125.67
125.65
125.32
77.32
77.00
76.68
73.93
35.86
21.86
21.47
15.66
O
N
3q
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

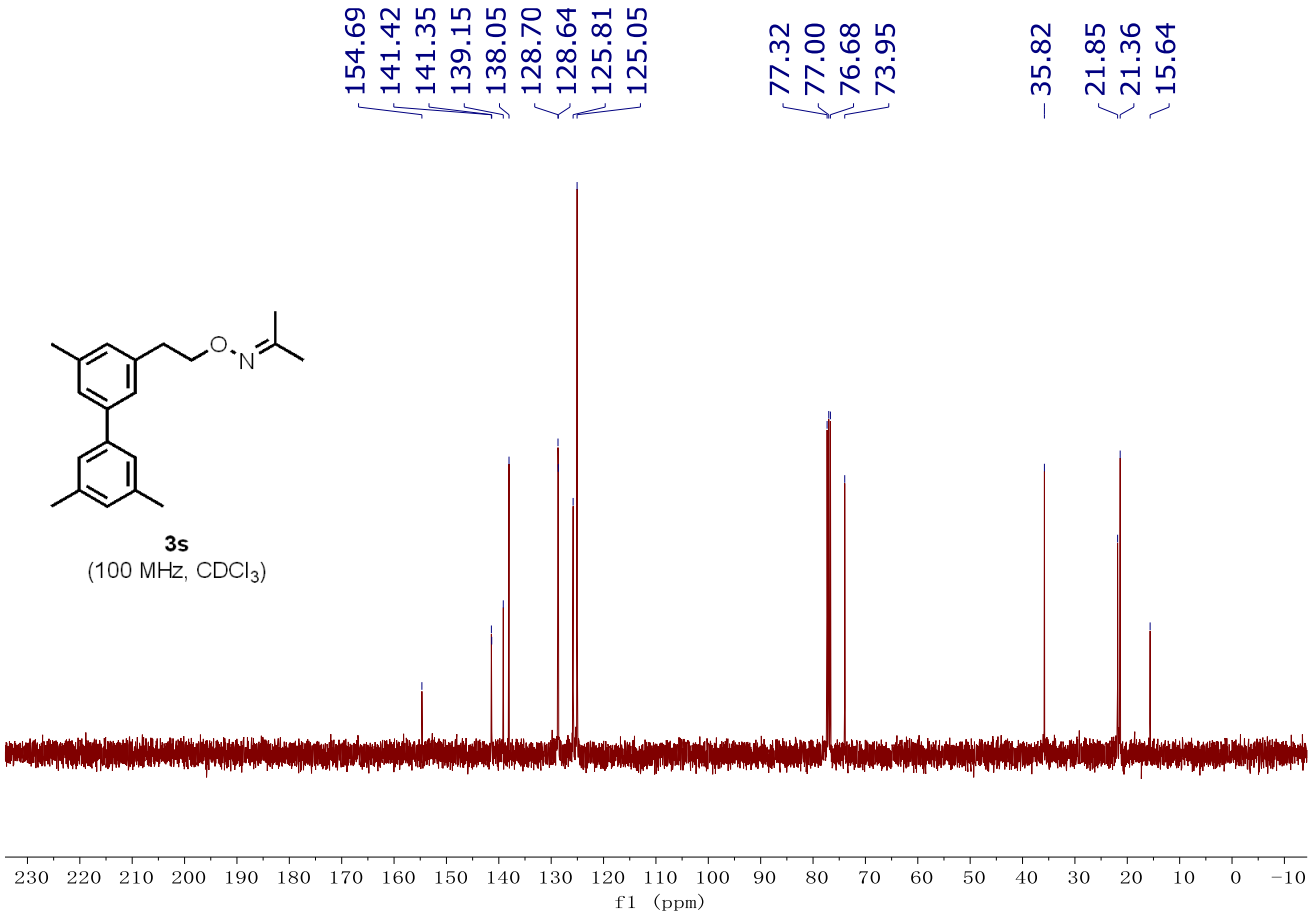

7.372
7.354
7.344
7.337
7.331
7.324
7.317
7.311
7.237
7.198
7.188
7.051
7.029
7.018
7.007
4.267
4.249
4.231
2.993
2.975
2.957
2.375
2.323
1.888
1.845
1.665
-0.000
O
N
F
3r
(400 MHz, CDCl3)
2.03
0.94
1.06
2.16
2.00
2.00
3.02
3.36
3.14
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)


162.12
159.69
154.79
140.42
139.33
138.25
137.18
137.14
130.20
130.14
128.67
125.91
125.83
125.66
124.89
124.73
115.18
114.96
77.32
77.00
76.68
73.90
35.79
21.85
21.41
15.64
14.67
14.63
O
N
F
3r
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

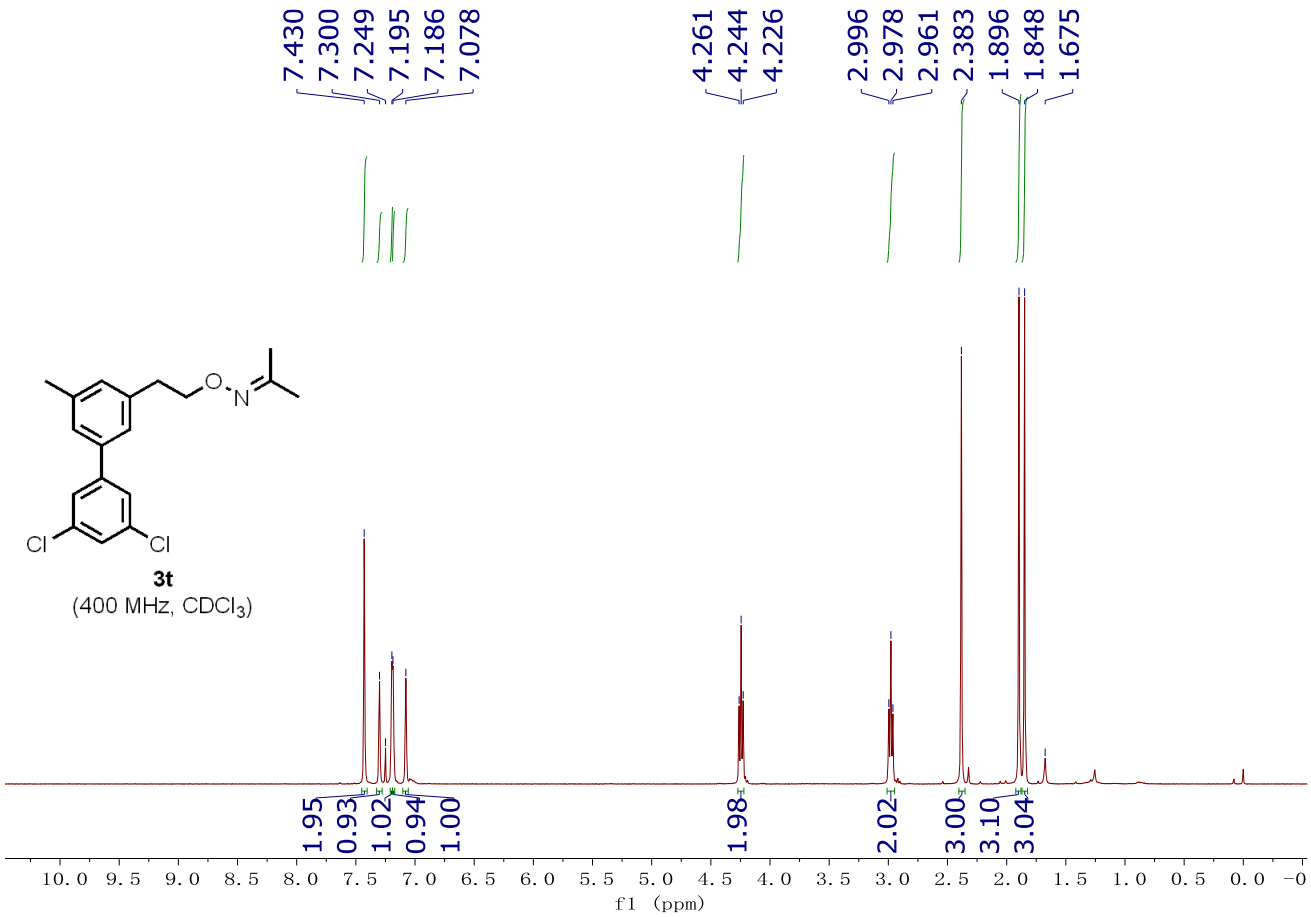

0.000
-120.864
-120.868
O
N
F
3r
(375 MHz, CDCl3)
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −2
f1 (ppm)

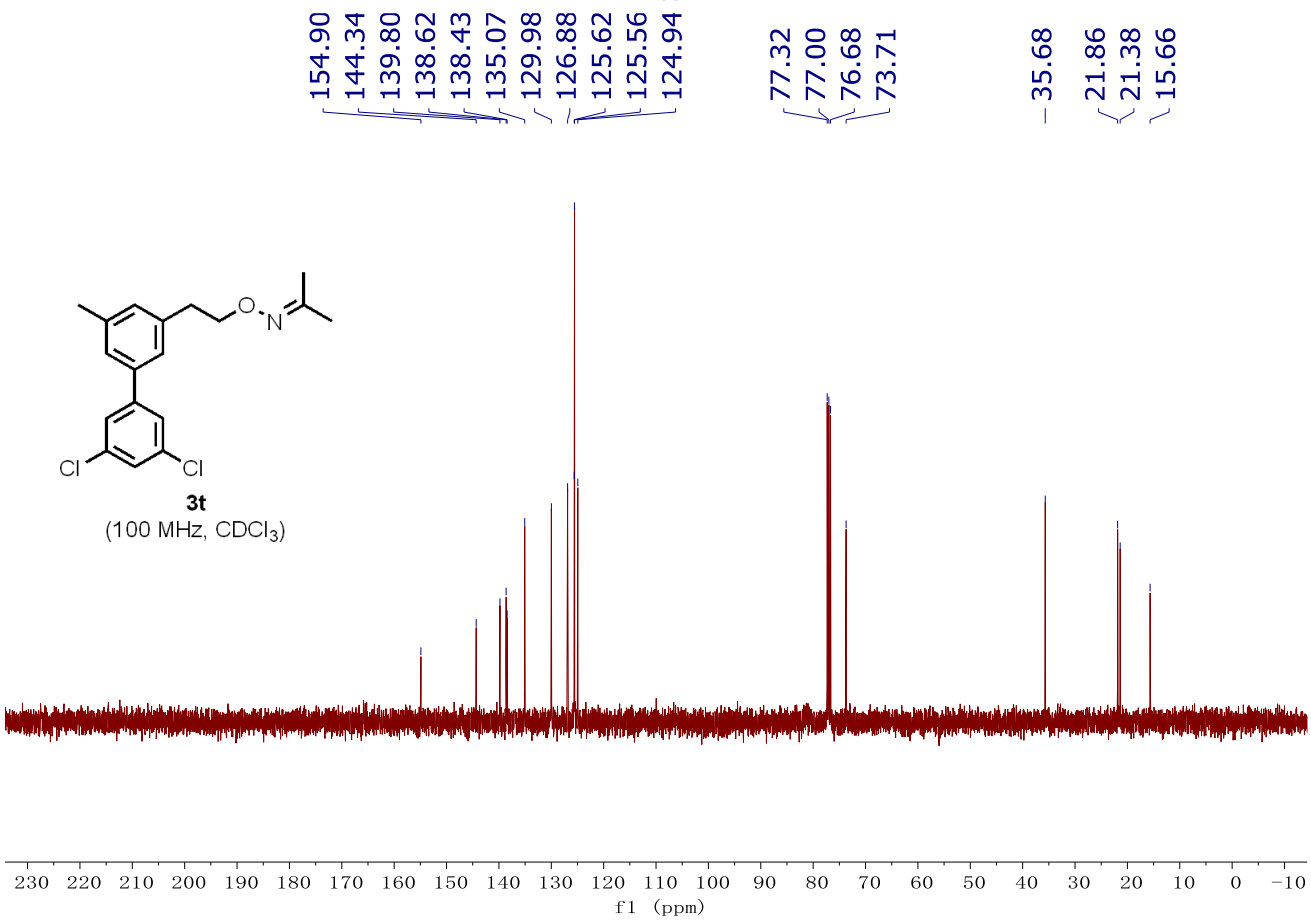


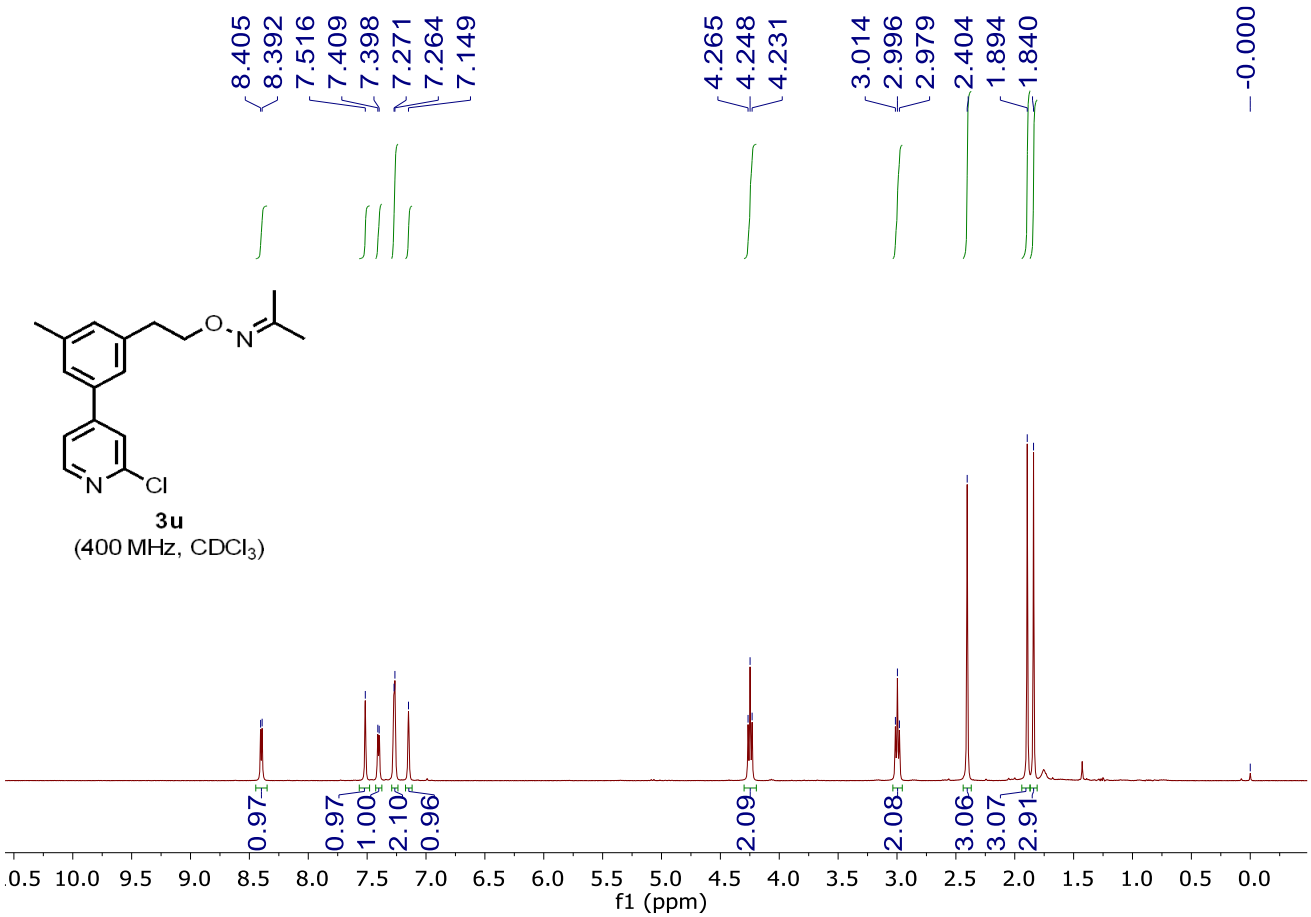
3s
(400 MHz, $CDCl_3$)

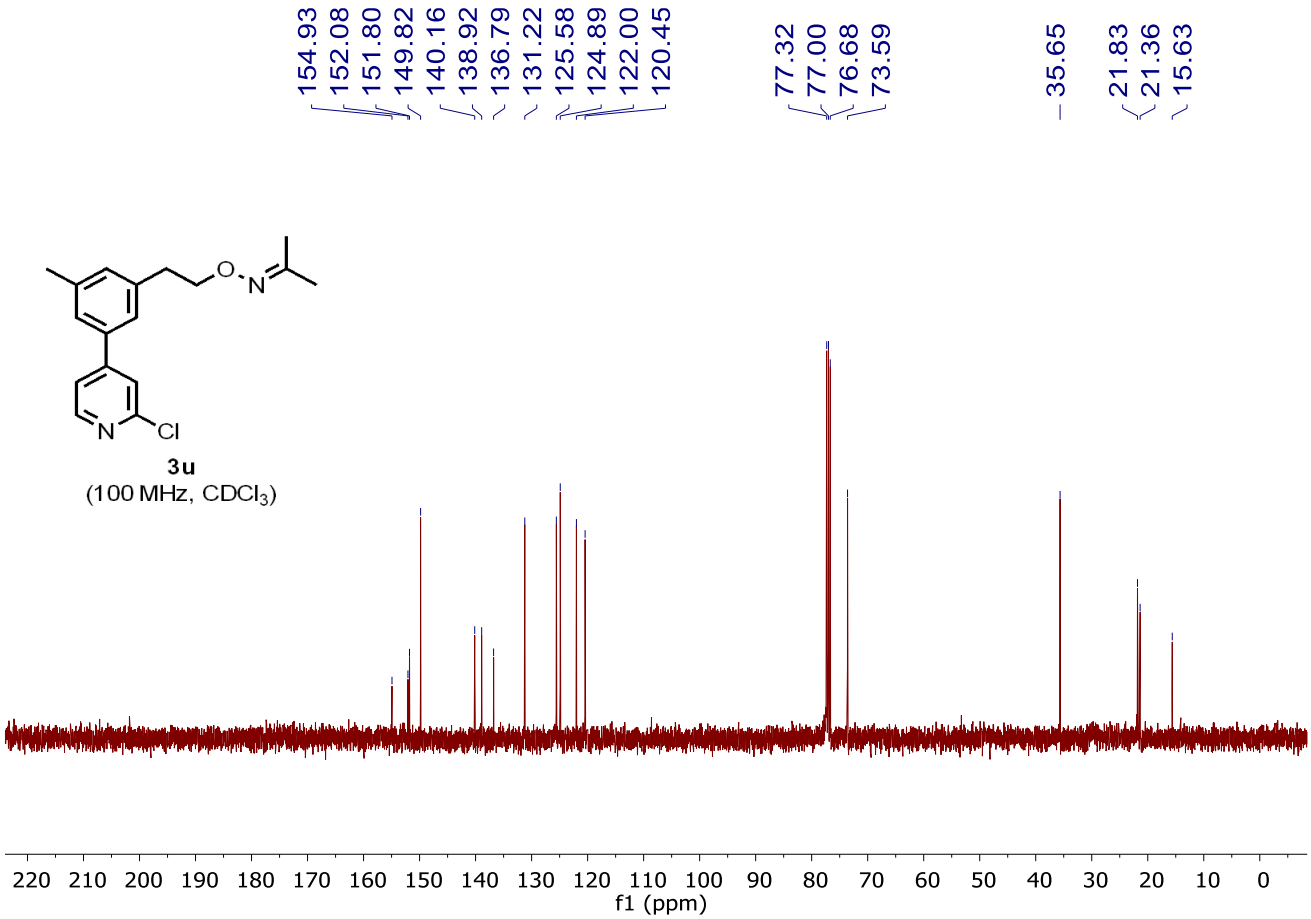


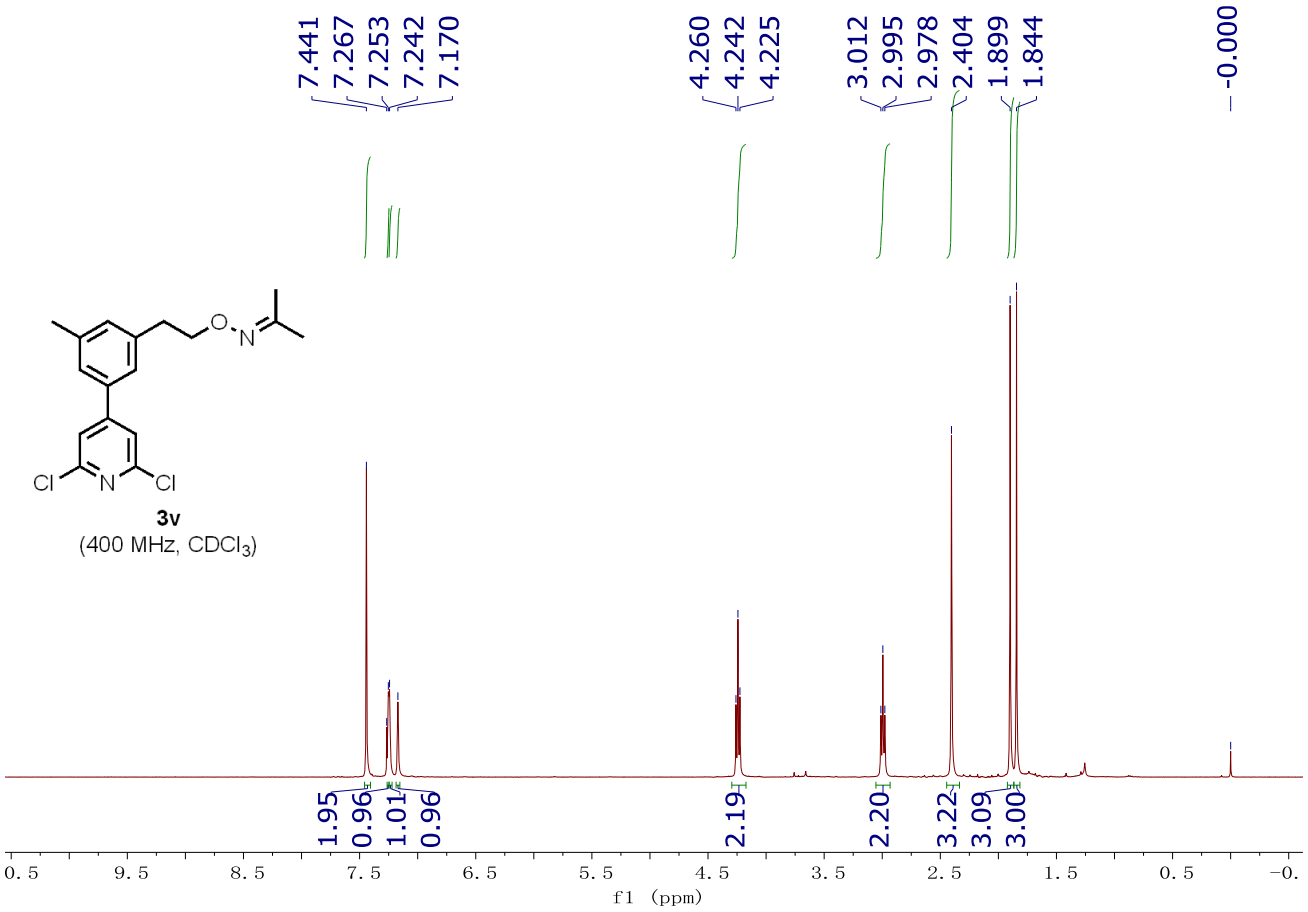
3s
(100 MHz, $CDCl_3$)


7.430
7.300
7.249
7.195
7.186
7.078
4.261
4.244
4.226
2.996
2.978
2.961
2.383
1.896
1.848
1.675
1.95
0.93
1.02
0.94
1.00
1.98
2.02
3.00
3.10
3.04
f1 (ppm)
3t
(400 MHz, CDCl3)

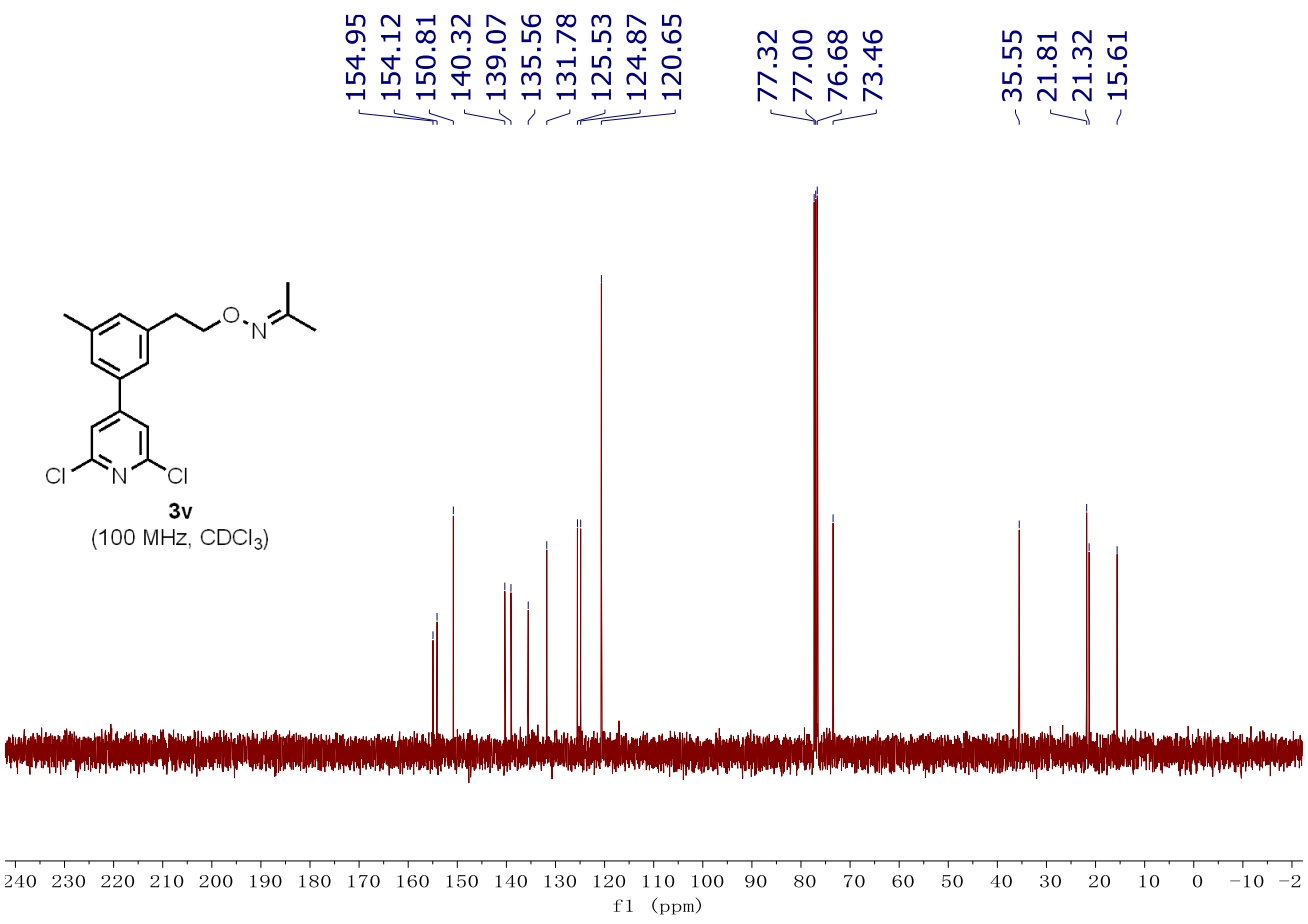

154.90
144.34
139.80
138.62
138.43
135.07
129.98
126.88
125.62
125.56
124.94
77.32
77.00
76.68
73.71
35.68
21.86
21.38
15.66
f1 (ppm)
3t
(100 MHz, CDCl3)


8.405
8.392
7.516
7.409
7.398
7.271
7.264
7.149
4.265
4.248
4.231
3.014
2.996
2.979
2.404
1.894
1.840
-0.000
O
N
N
Cl
3u
(400 MHz, CDCl3)
0.97
0.97
1.00
2.10
0.96
2.09
2.08
3.06
3.07
2.91
f1 (ppm)

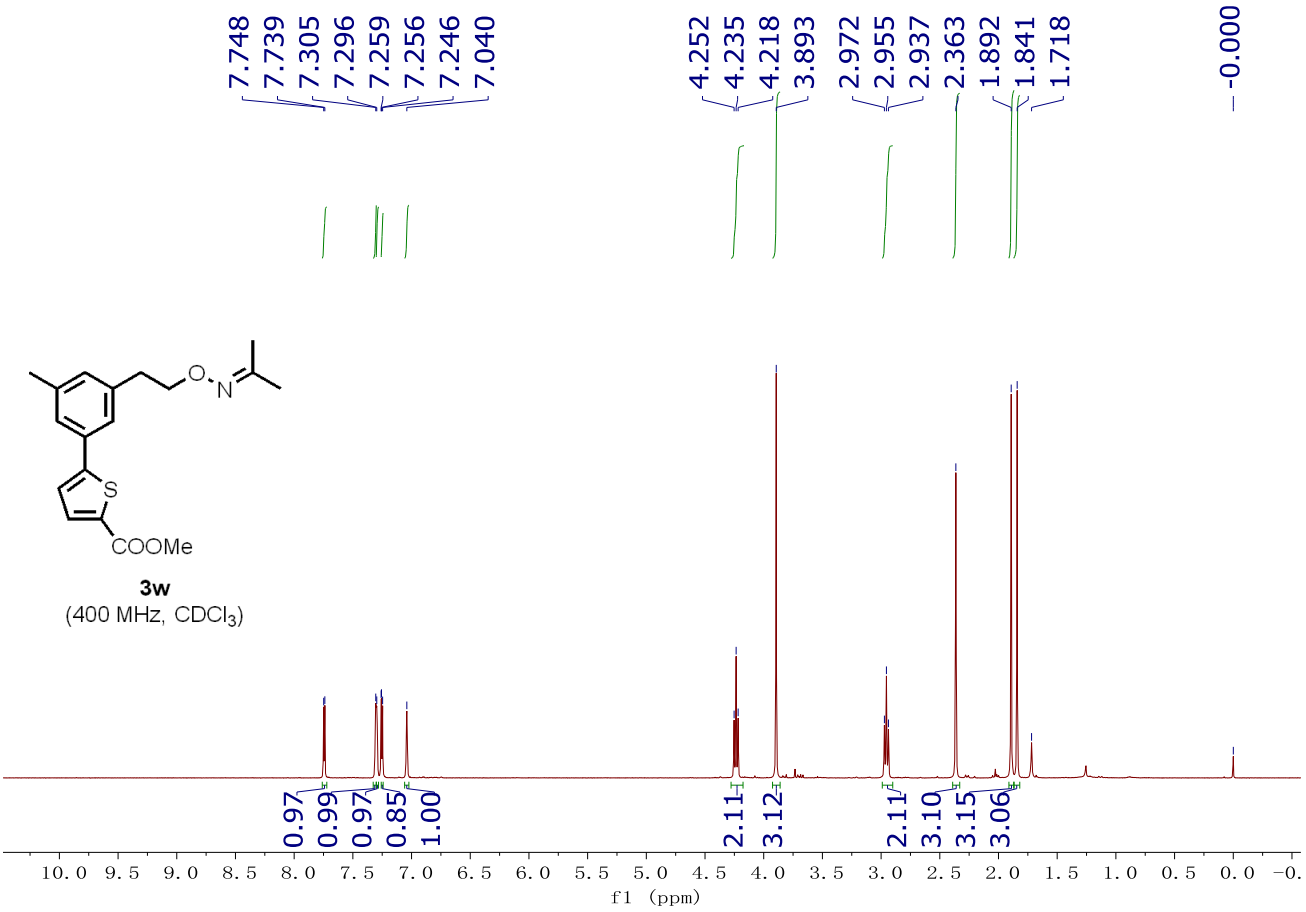

154.93
152.08
151.80
149.82
140.16
138.92
136.79
131.22
125.58
124.89
122.00
120.45
77.32
77.00
76.68
73.59
35.65
21.83
21.36
15.63
O
N
N
Cl
3u
(100 MHz, CDCl3)
f1 (ppm)

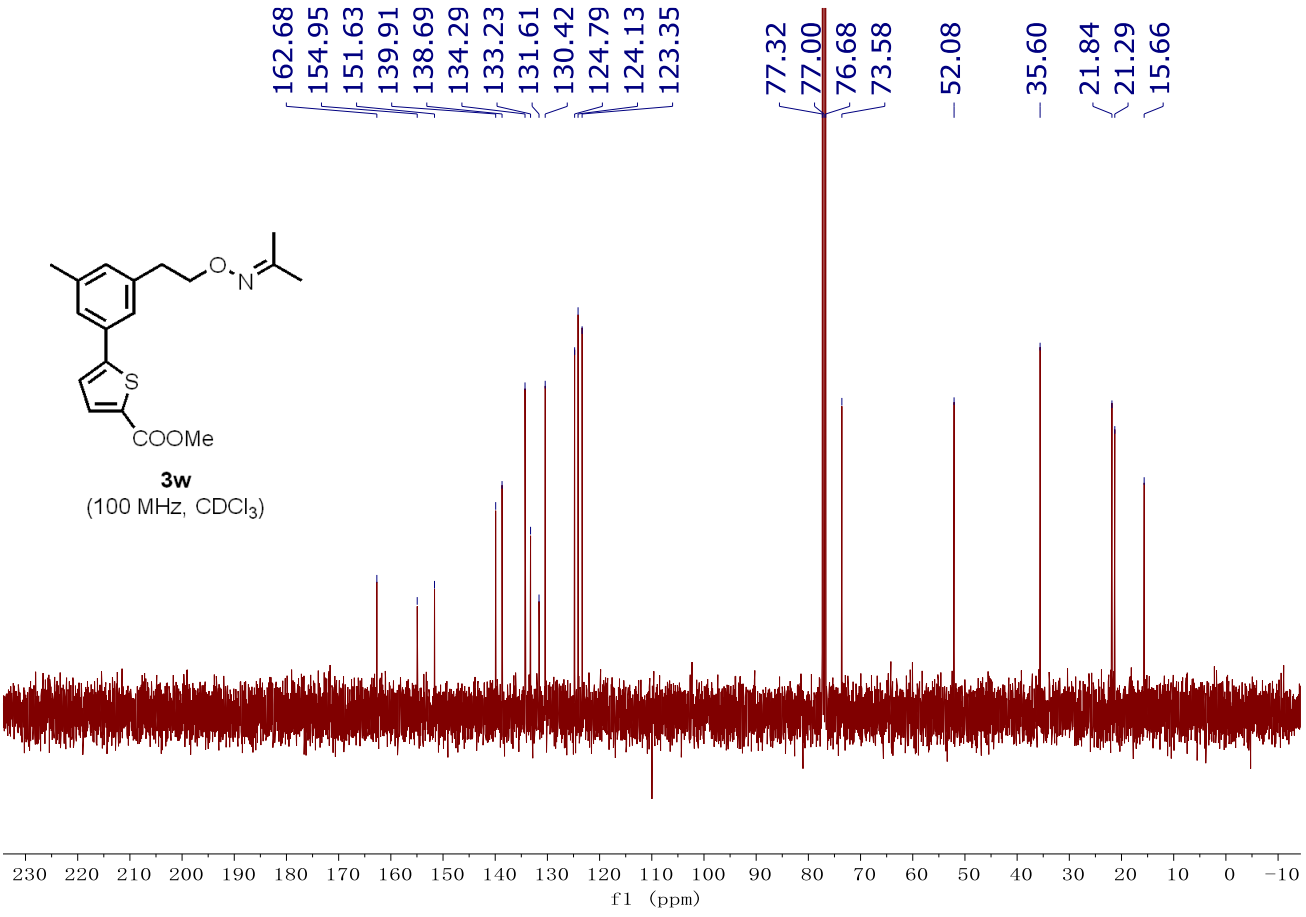


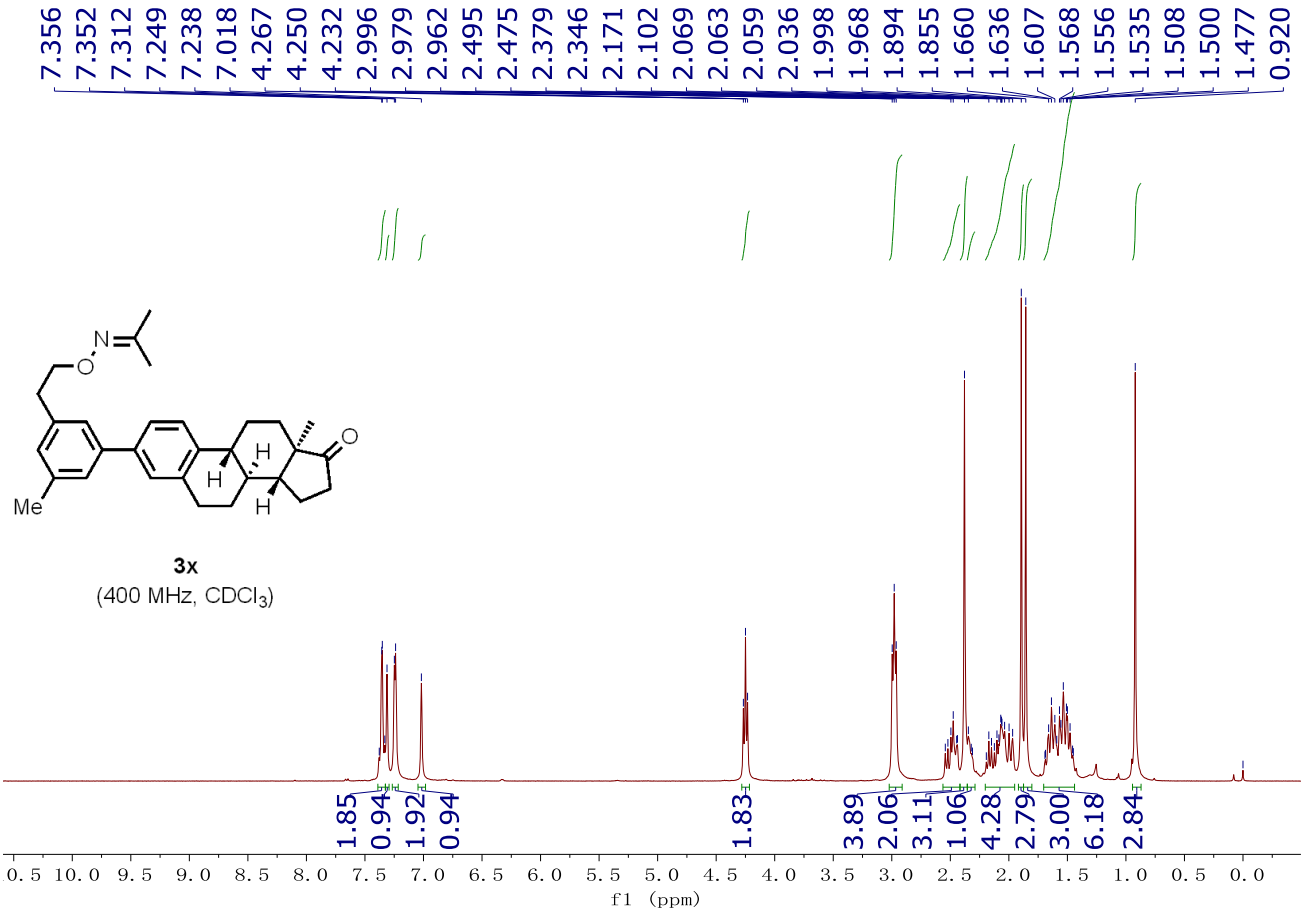
3v
(400 MHz, $CDCl_3$)

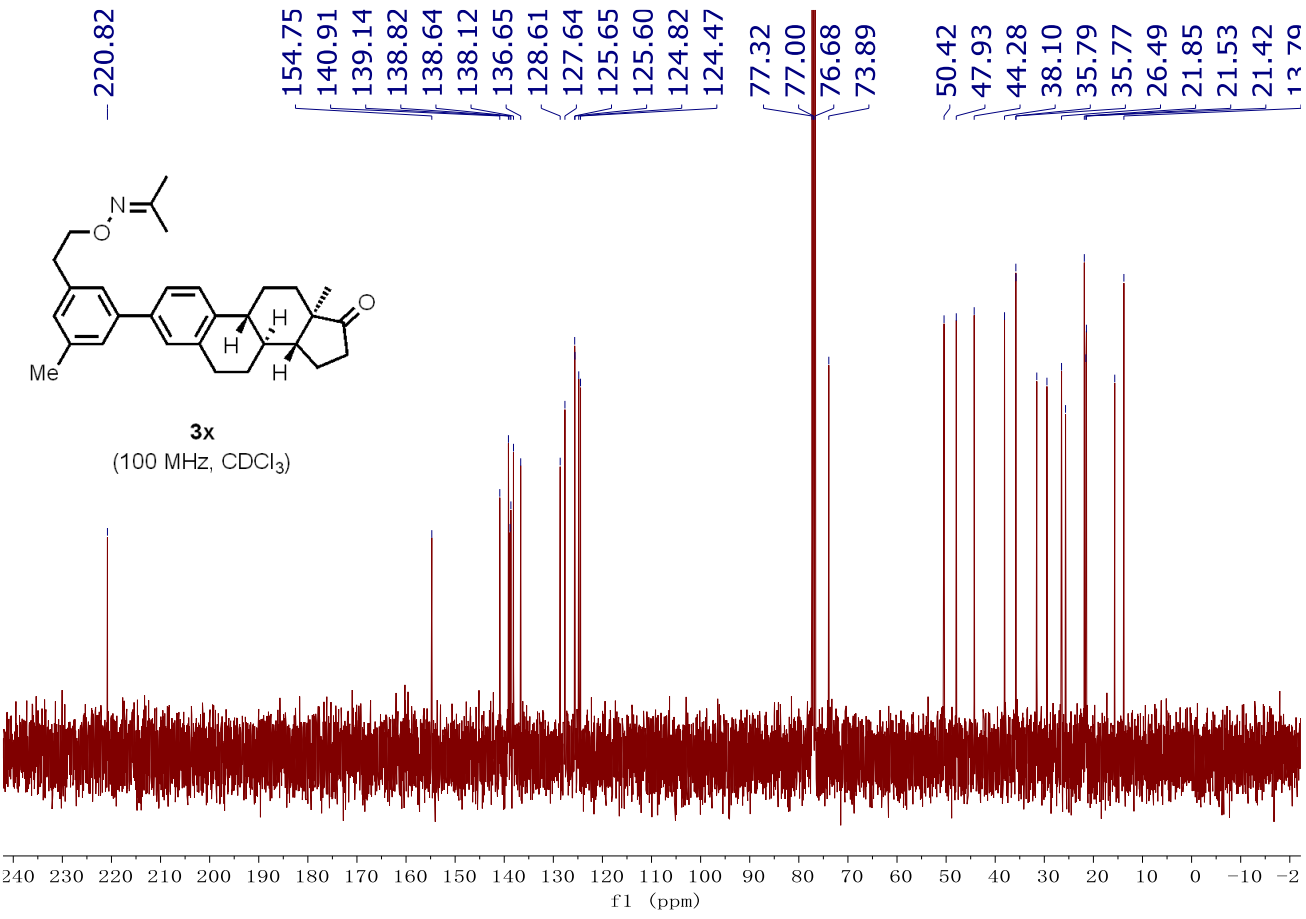


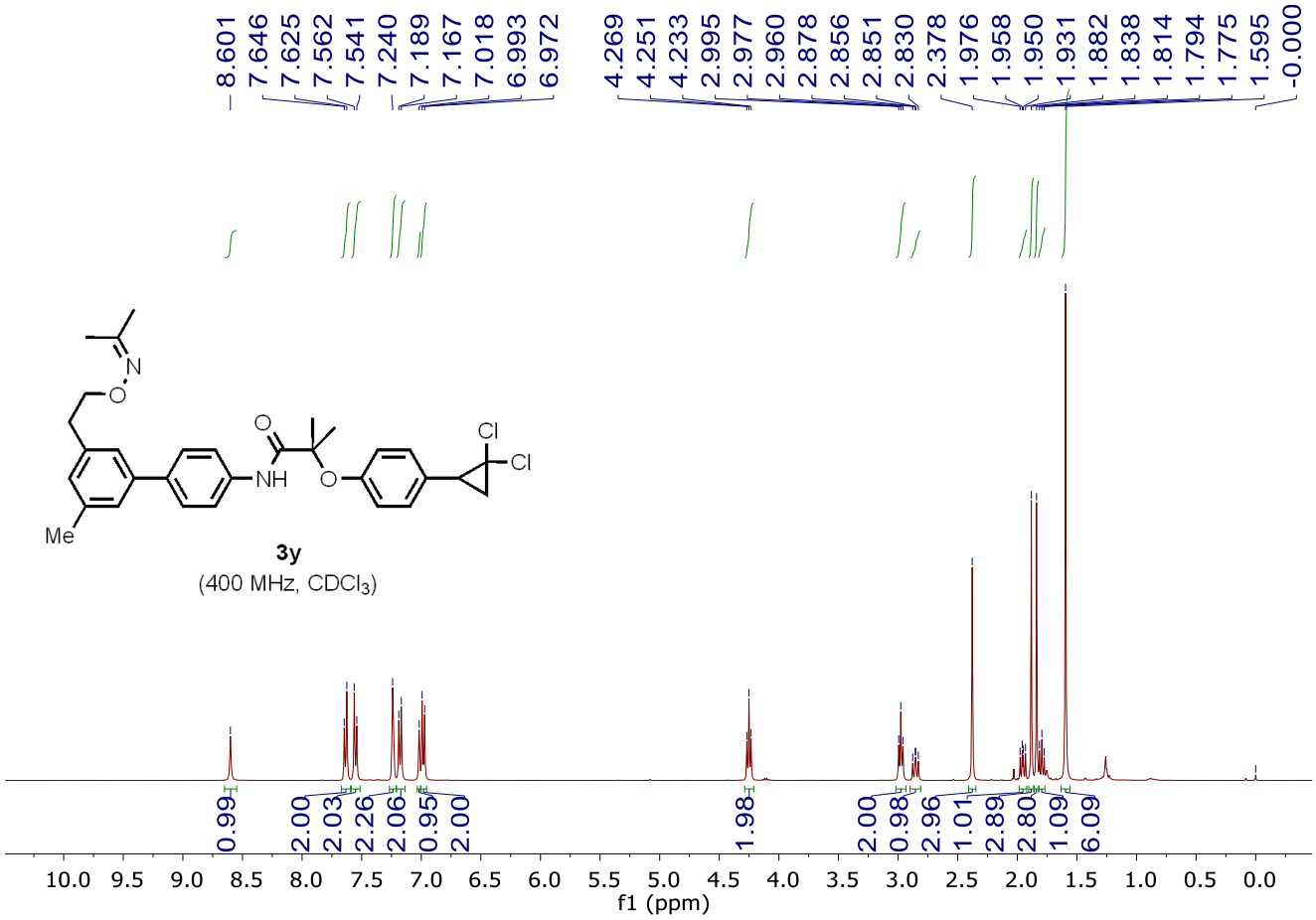
3v
(100 MHz, $CDCl_3$)

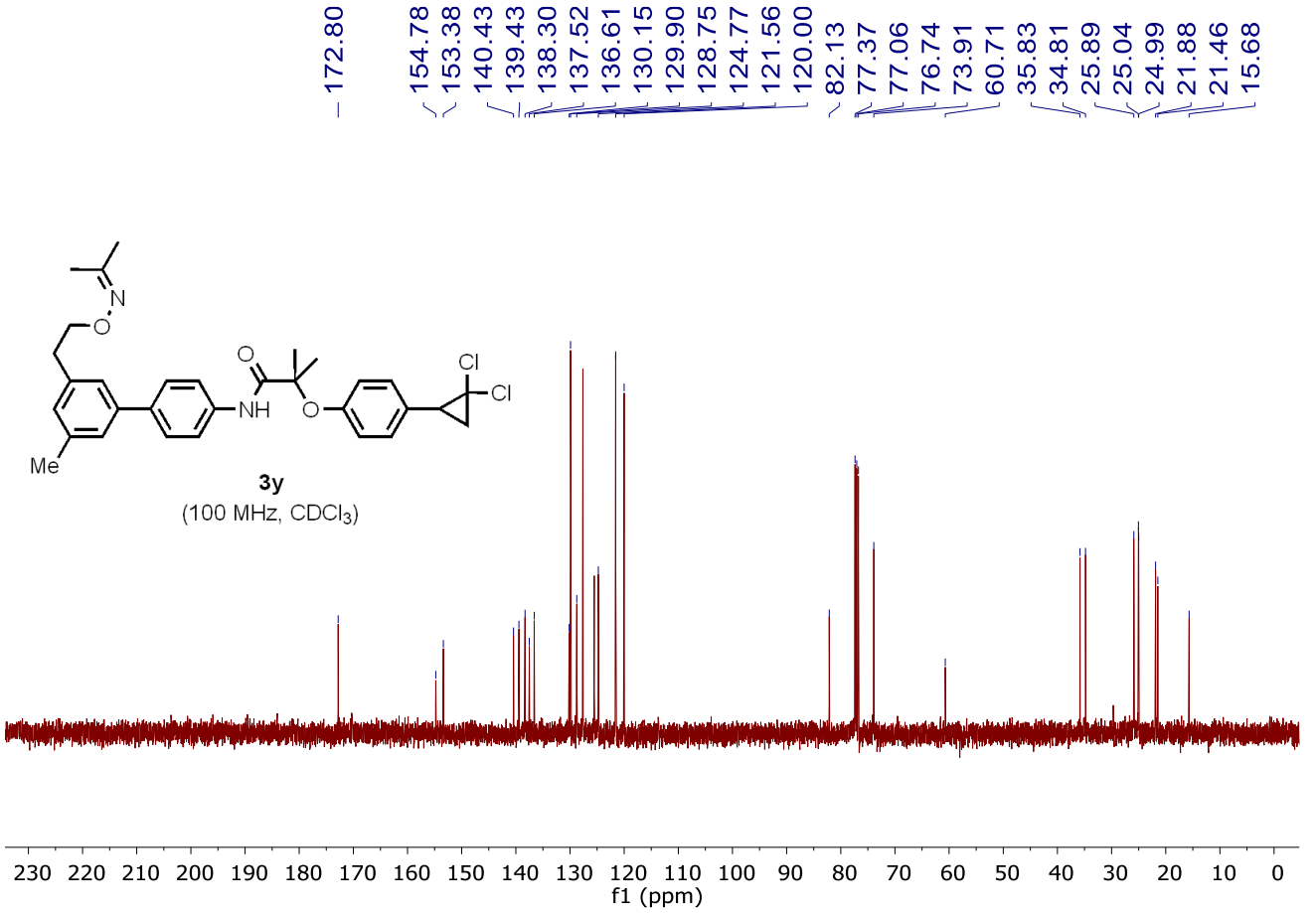

7.748
7.739
7.305
7.296
7.259
7.256
7.246
7.040
4.252
4.235
4.218
3.893
2.972
2.955
2.937
2.363
1.892
1.841
1.718
-0.000
COOMe
3w
(400 MHz, CDCl3)
0.97
0.99
0.97
0.85
1.00
2.11
3.12
2.11
3.10
3.15
3.06
f1 (ppm)

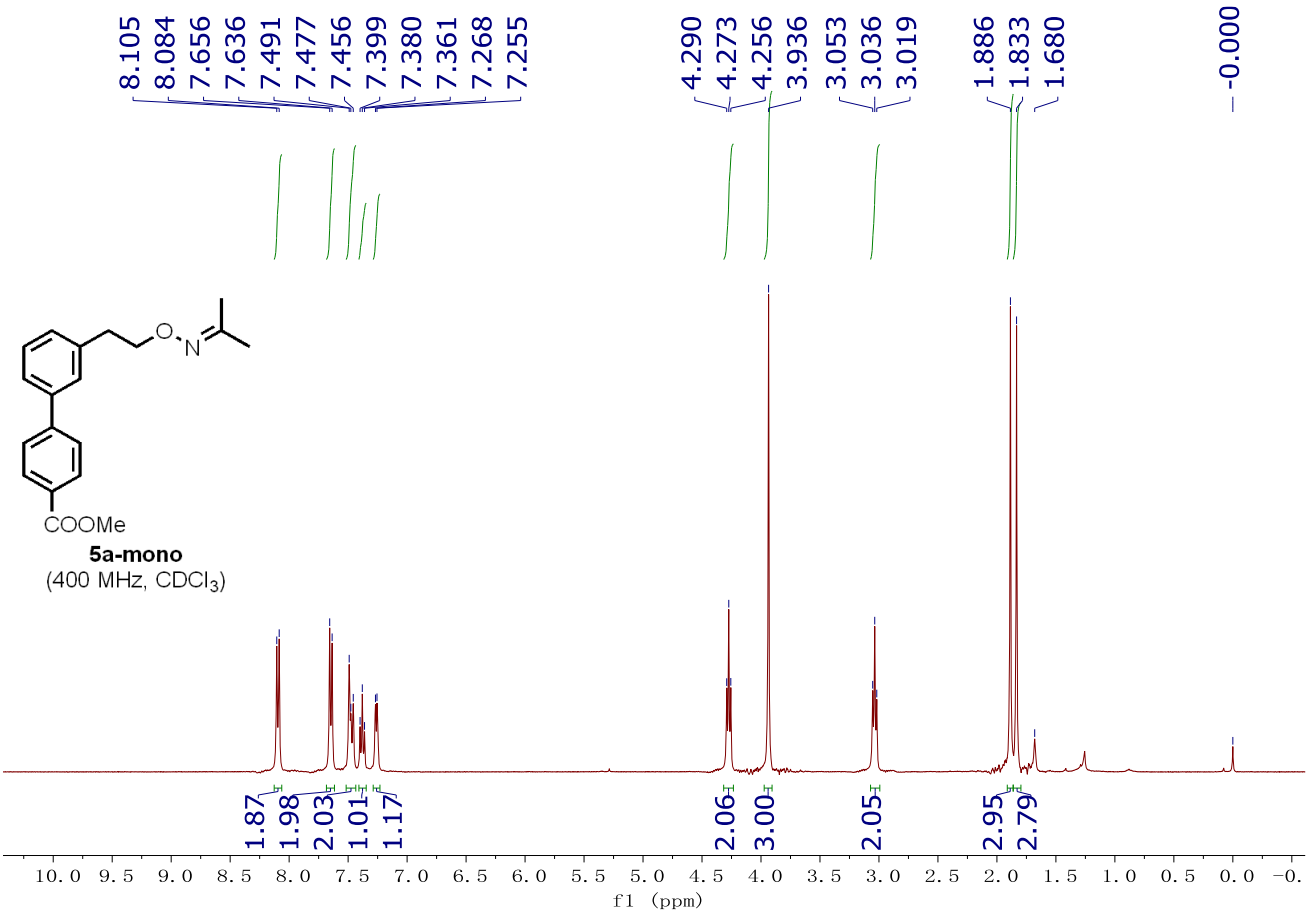

162.68
154.95
151.63
139.91
138.69
134.29
133.23
131.61
130.42
124.79
124.13
123.35
77.32
77.00
76.68
73.58
52.08
35.60
21.84
21.29
15.66
COOMe
3w
(100 MHz, CDCl3)
f1 (ppm)

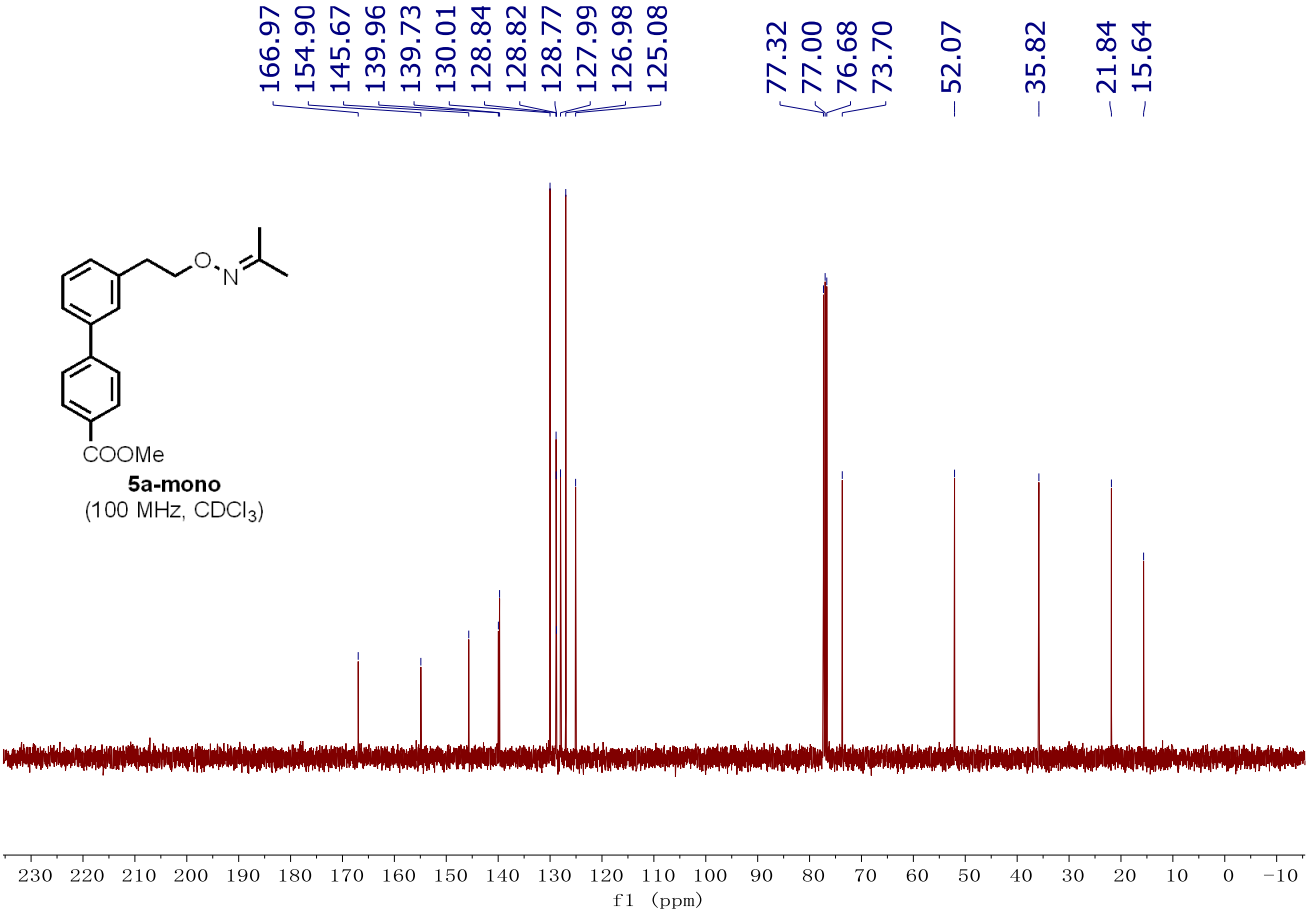

7.356
7.352
7.312
7.249
7.238
7.018
4.267
4.250
4.232
2.996
2.979
2.962
2.495
2.475
2.379
2.346
2.171
2.102
2.069
2.063
2.059
2.036
1.998
1.968
1.894
1.855
1.660
1.636
1.607
1.568
1.556
1.535
1.508
1.500
1.477
0.920
Me
3x
(400 MHz, CDCl3)
1.85
0.94
1.92
0.94
1.83
3.89
2.06
3.11
1.06
4.28
2.79
3.00
6.18
2.84
f1 (ppm)

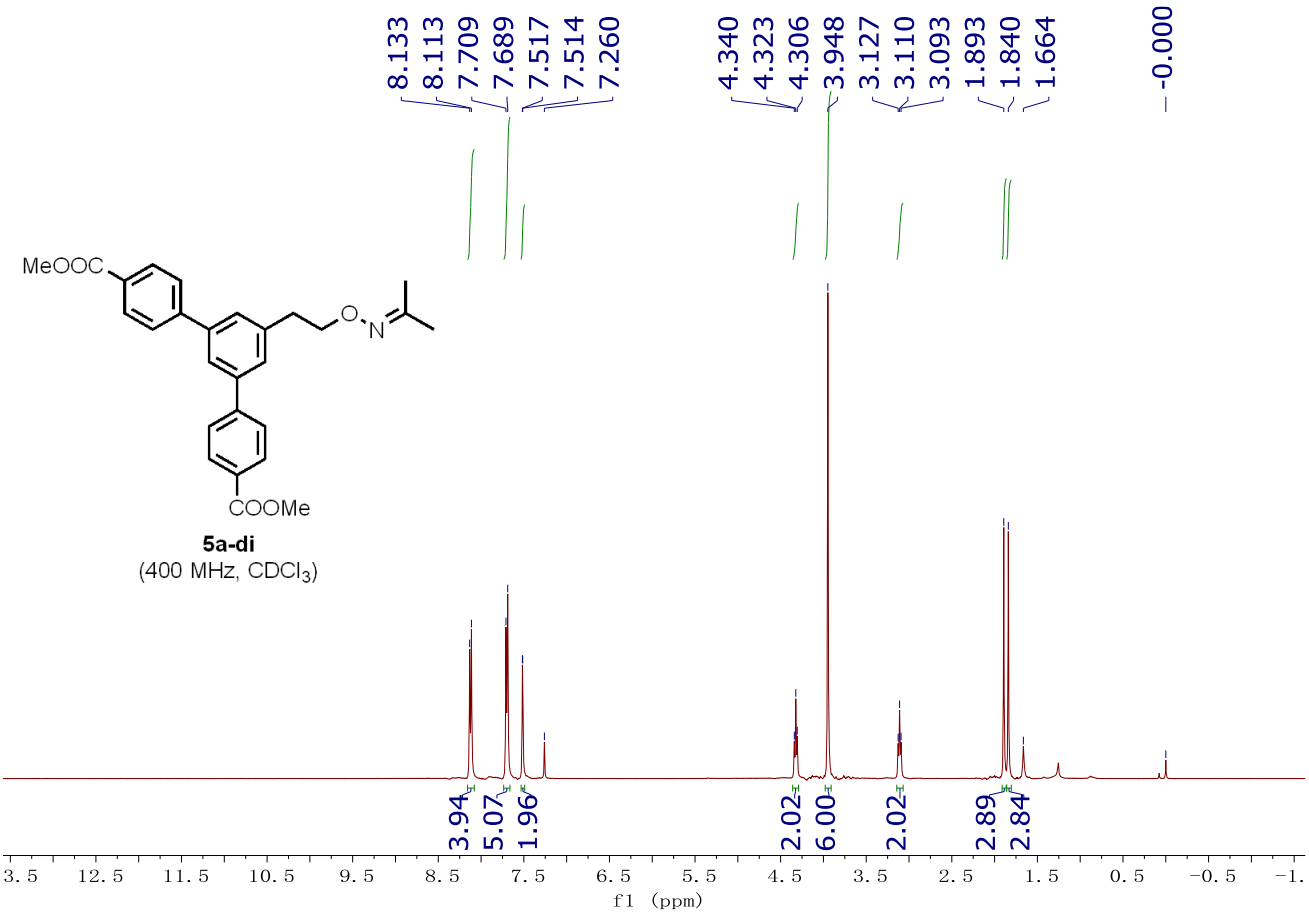

220.82
154.75
140.91
139.14
138.82
138.64
138.12
136.65
128.61
127.64
125.65
125.60
124.82
124.47
77.32
77.00
76.68
73.89
50.42
47.93
44.28
38.10
35.79
35.77
26.49
21.85
21.53
21.42
Me
3x
(100 MHz, CDCl3)
f1 (ppm)

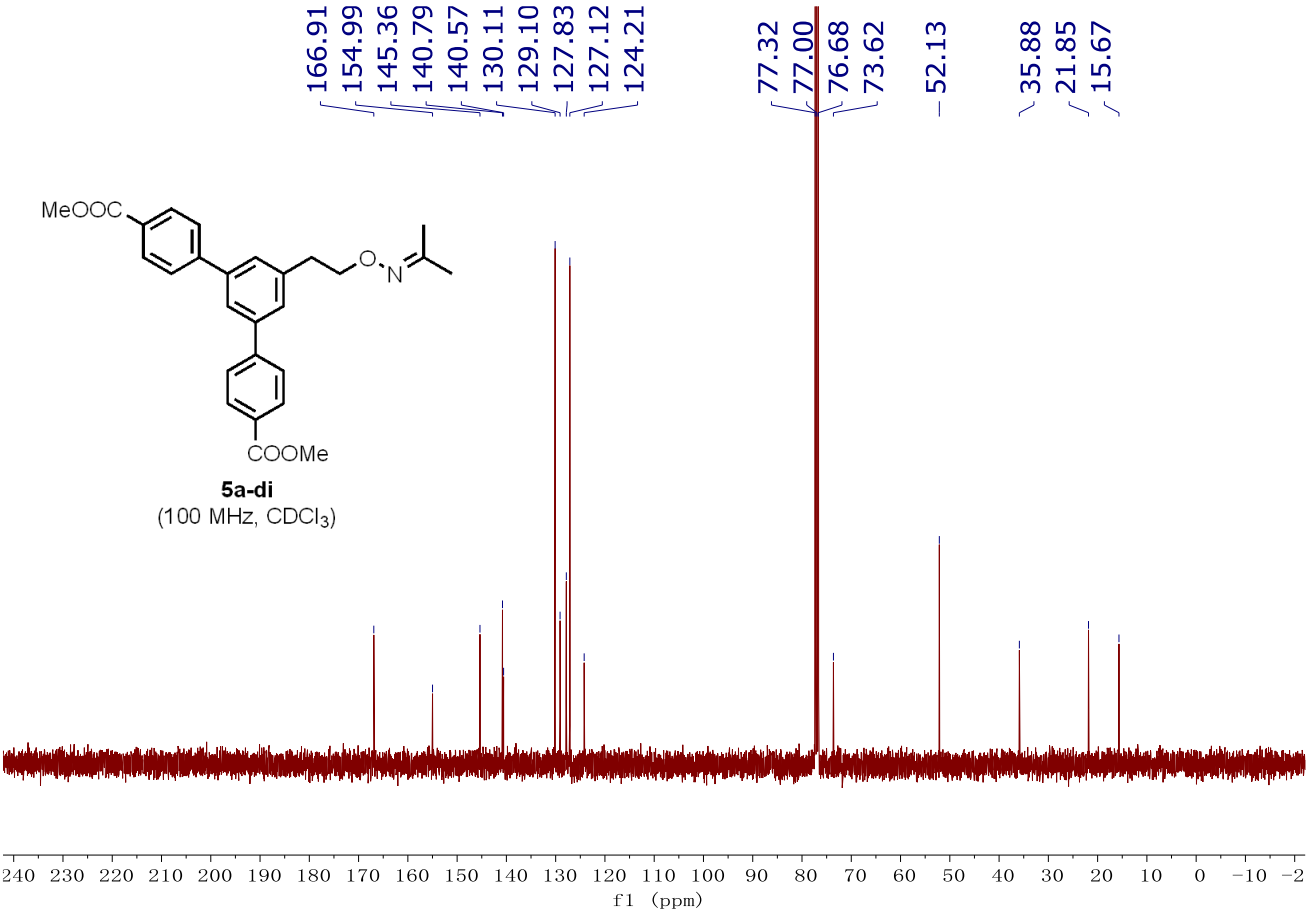

8.601
7.646
7.625
7.562
7.541
7.240
7.189
7.167
7.018
6.993
6.972
4.269
4.251
4.233
2.995
2.977
2.960
2.878
2.856
2.851
2.830
2.378
1.976
1.958
1.950
1.931
1.882
1.838
1.814
1.794
1.775
1.595
-0.000
Me
NH
O
Cl
Cl
3y
(400 MHz, CDCl3)
0.99
2.00
2.03
2.26
2.06
0.95
2.00
1.98
2.00
0.98
2.96
1.01
2.89
2.80
1.09
6.09
f1 (ppm)

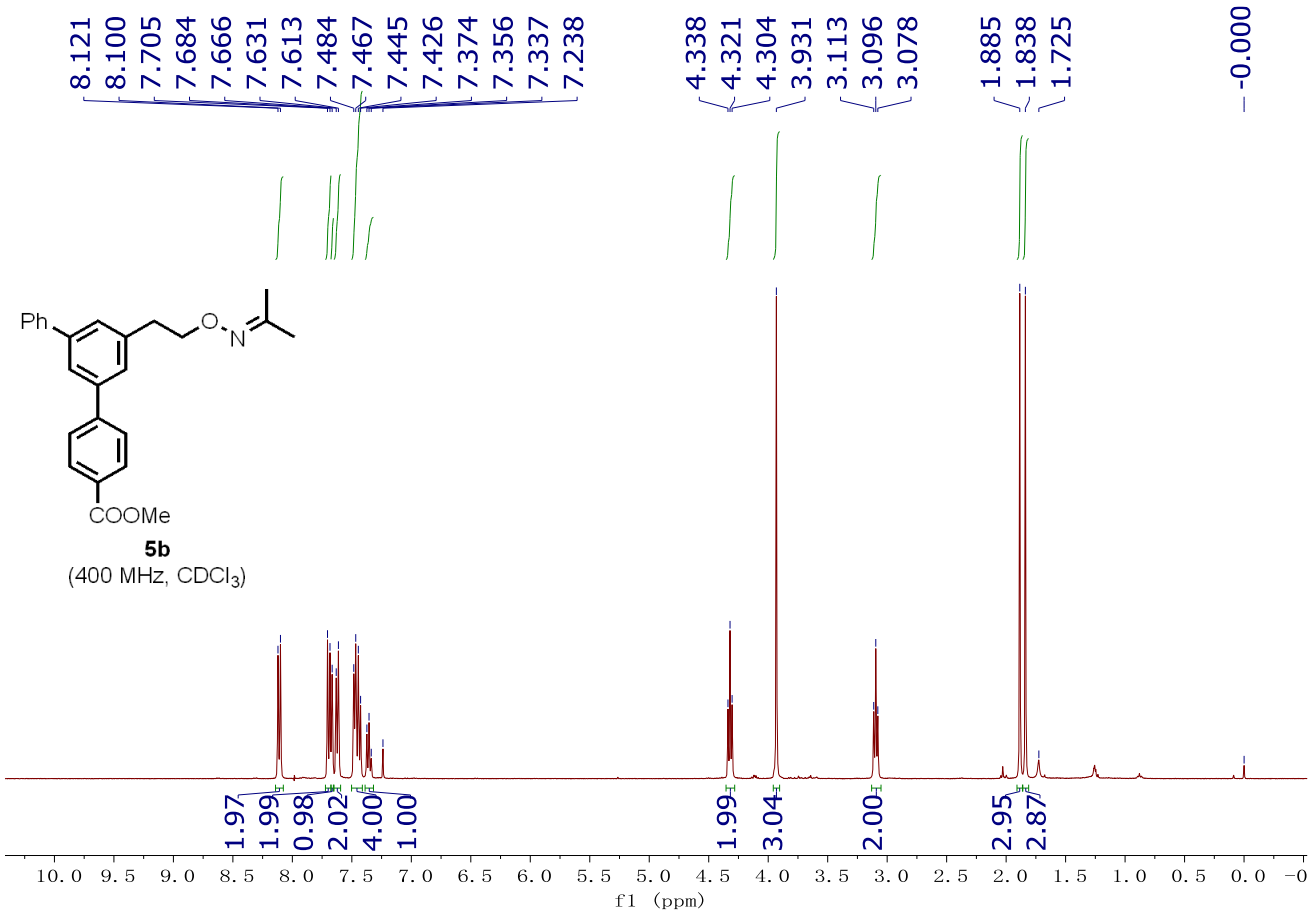

172.80
154.78
153.38
140.43
139.43
138.30
137.52
136.61
130.15
129.90
128.75
124.77
121.56
120.00
82.13
77.37
77.06
76.74
73.91
60.71
35.83
34.81
25.89
25.04
24.99
21.88
21.46
15.68
Me
NH
O
Cl
Cl
3y
(100 MHz, CDCl3)
f1 (ppm)

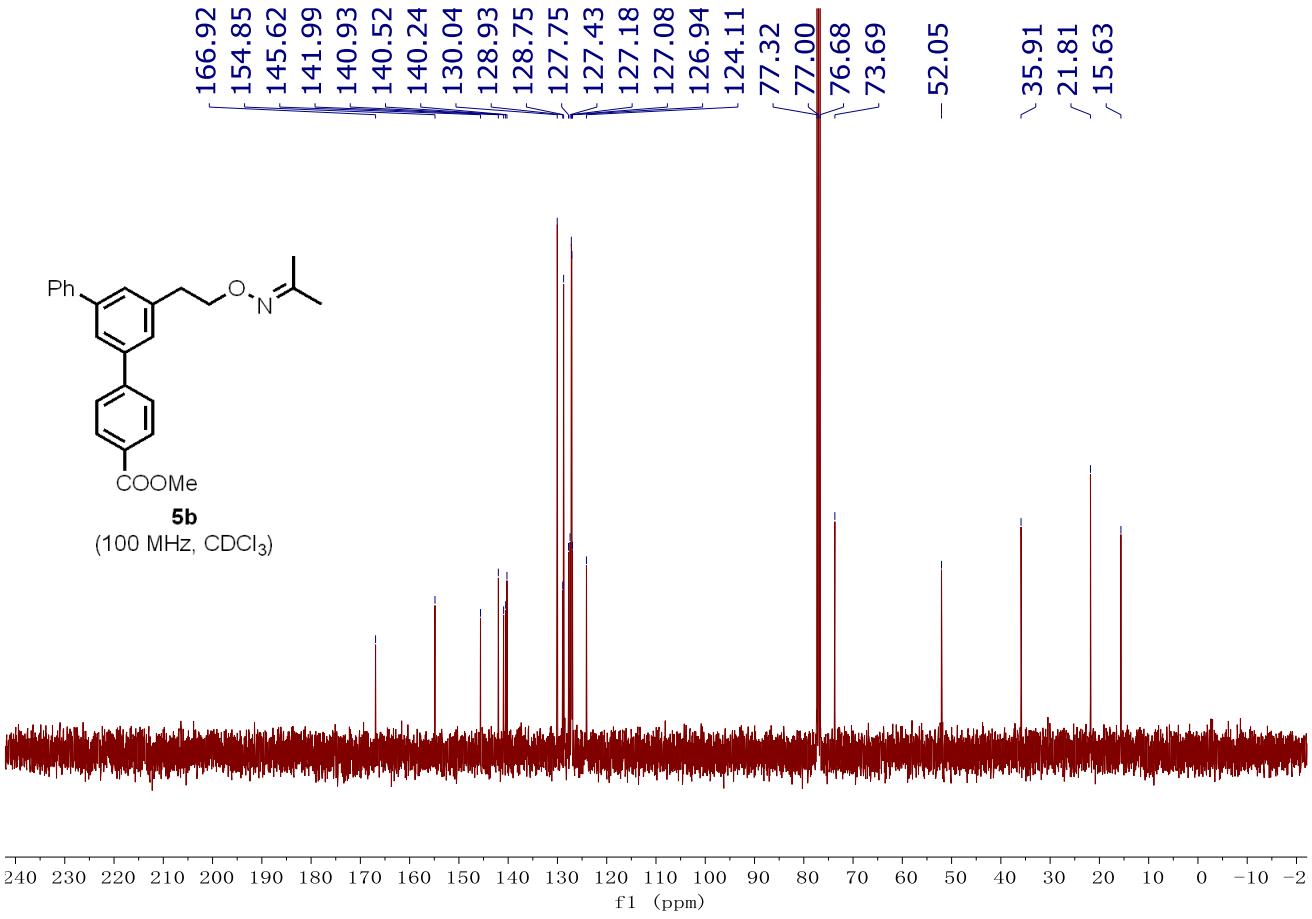

8.105
8.084
7.656
7.636
7.491
7.477
7.456
7.399
7.380
7.361
7.268
7.255
4.290
4.273
4.256
3.936
3.053
3.036
3.019
1.886
1.833
1.680
-0.000
COOMe
5a-mono
(400 MHz, CDCl3)
1.87
1.98
2.03
1.01
1.17
2.06
3.00
2.05
2.95
2.79
f1 (ppm)

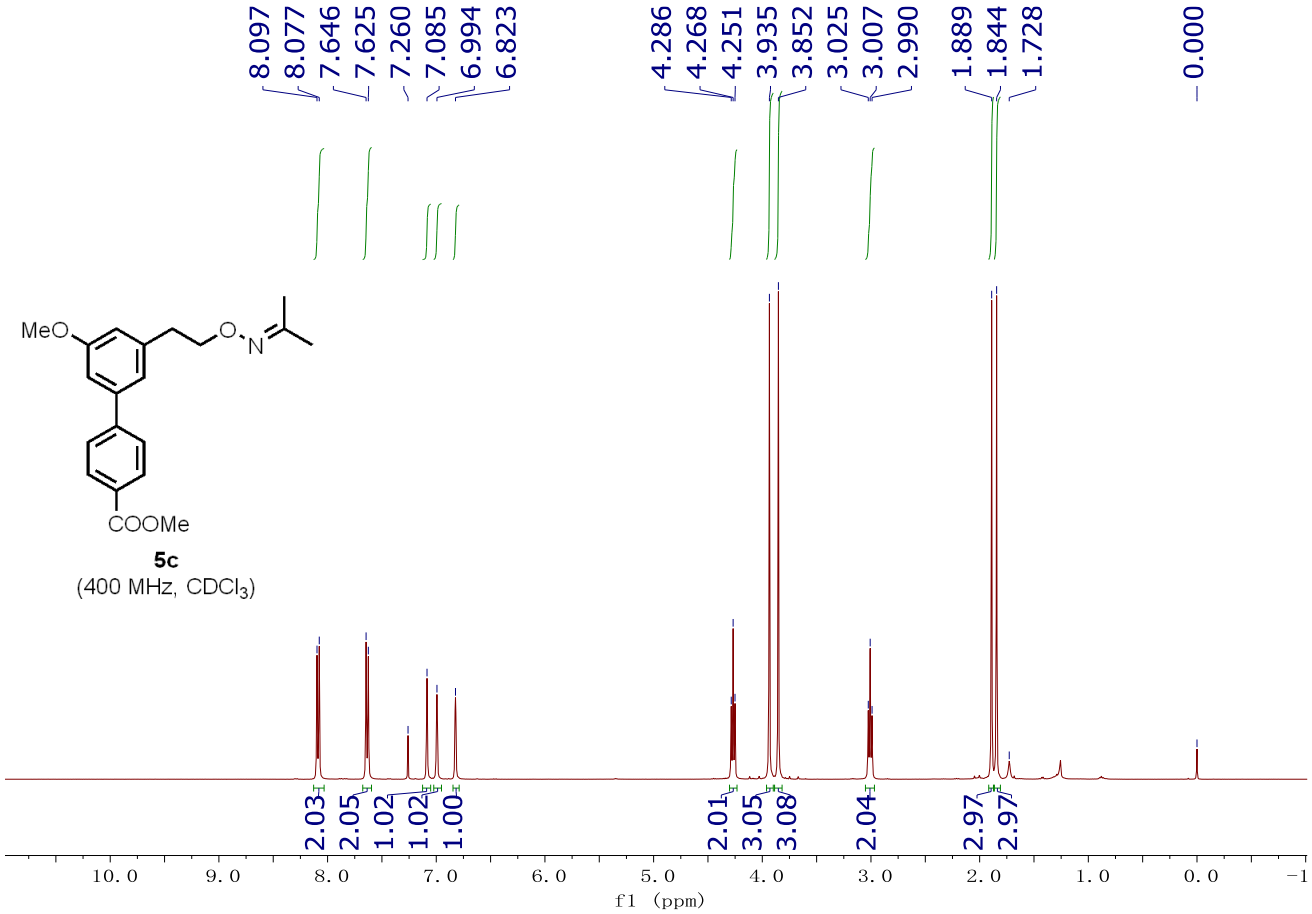

166.97
154.90
145.67
139.96
139.73
130.01
128.84
128.82
128.77
127.99
126.98
125.08
77.32
77.00
76.68
73.70
52.07
35.82
21.84
15.64
COOMe
5a-mono
(100 MHz, CDCl3)
f1 (ppm)


8.133
8.113
7.709
7.689
7.517
7.514
7.260
4.340
4.323
4.306
3.948
3.127
3.110
3.093
1.893
1.840
1.664
-0.000
MeOOC
O
N
COOMe
5a-di
(400 MHz, CDCl3)
3.94
5.07
1.96
2.02
6.00
2.02
2.89
2.84
f1 (ppm)

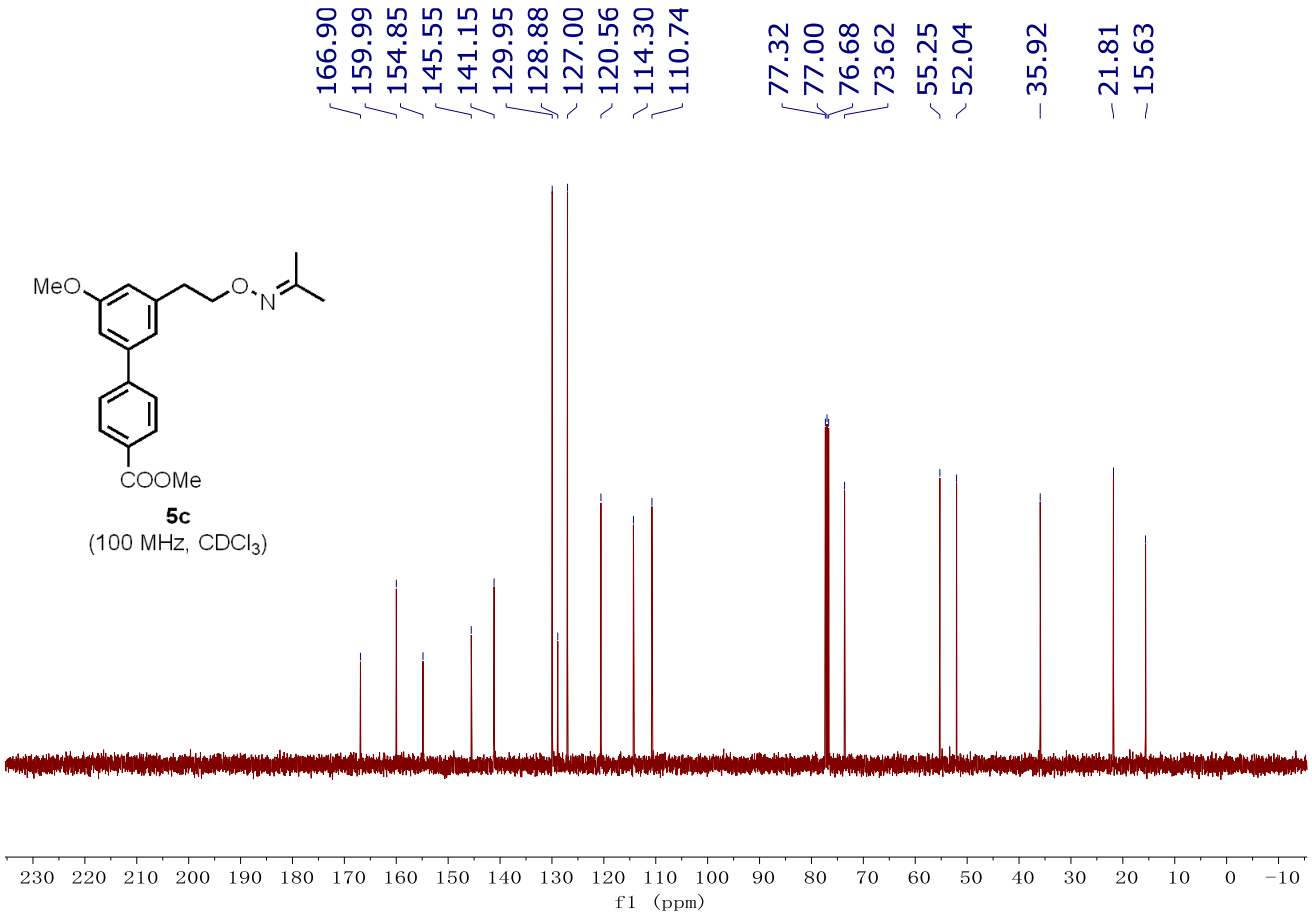

166.91
154.99
145.36
140.79
140.57
130.11
129.10
127.83
127.12
124.21
77.32
77.00
76.68
73.62
52.13
35.88
21.85
15.67
MeOOC
O
N
COOMe
5a-di
(100 MHz, CDCl3)
f1 (ppm)


8.121
8.100
7.705
7.684
7.666
7.631
7.613
7.484
7.467
7.445
7.426
7.374
7.356
7.337
7.238
4.338
4.321
4.304
3.931
3.113
3.096
3.078
1.885
1.838
1.725
-0.000
Ph
O
N
COOMe
5b
(400 MHz, CDCl3)
1.97
1.99
0.98
2.02
4.00
1.00
1.99
3.04
2.00
2.95
2.87
f1 (ppm)

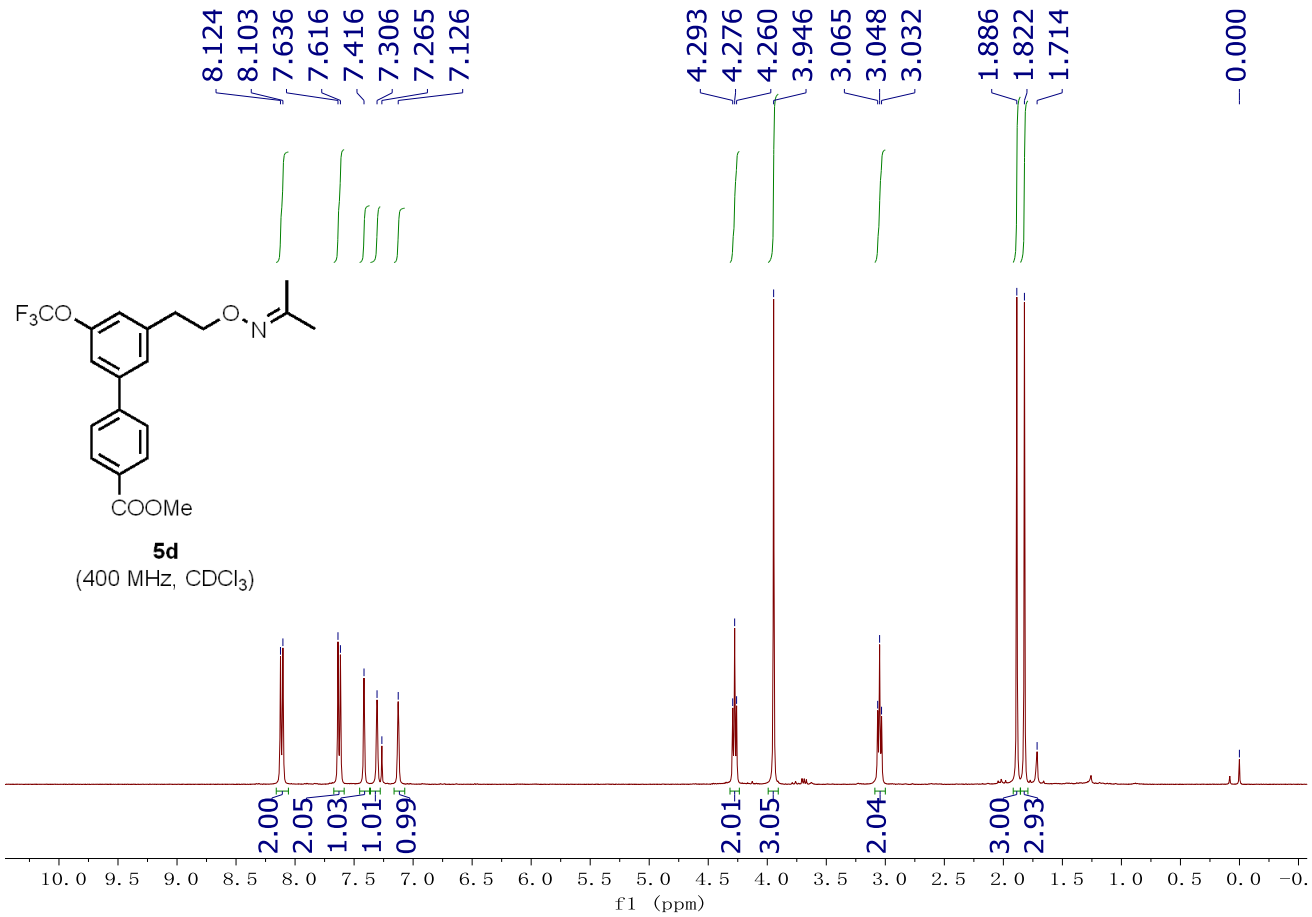

166.92
154.85
145.62
141.99
140.93
140.52
140.24
130.04
128.93
128.75
127.75
127.43
127.18
127.08
126.94
124.11
77.32
77.00
76.68
73.69
52.05
35.91
21.81
15.63
Ph
O
N
COOMe
5b
(100 MHz, CDCl3)
f1 (ppm)

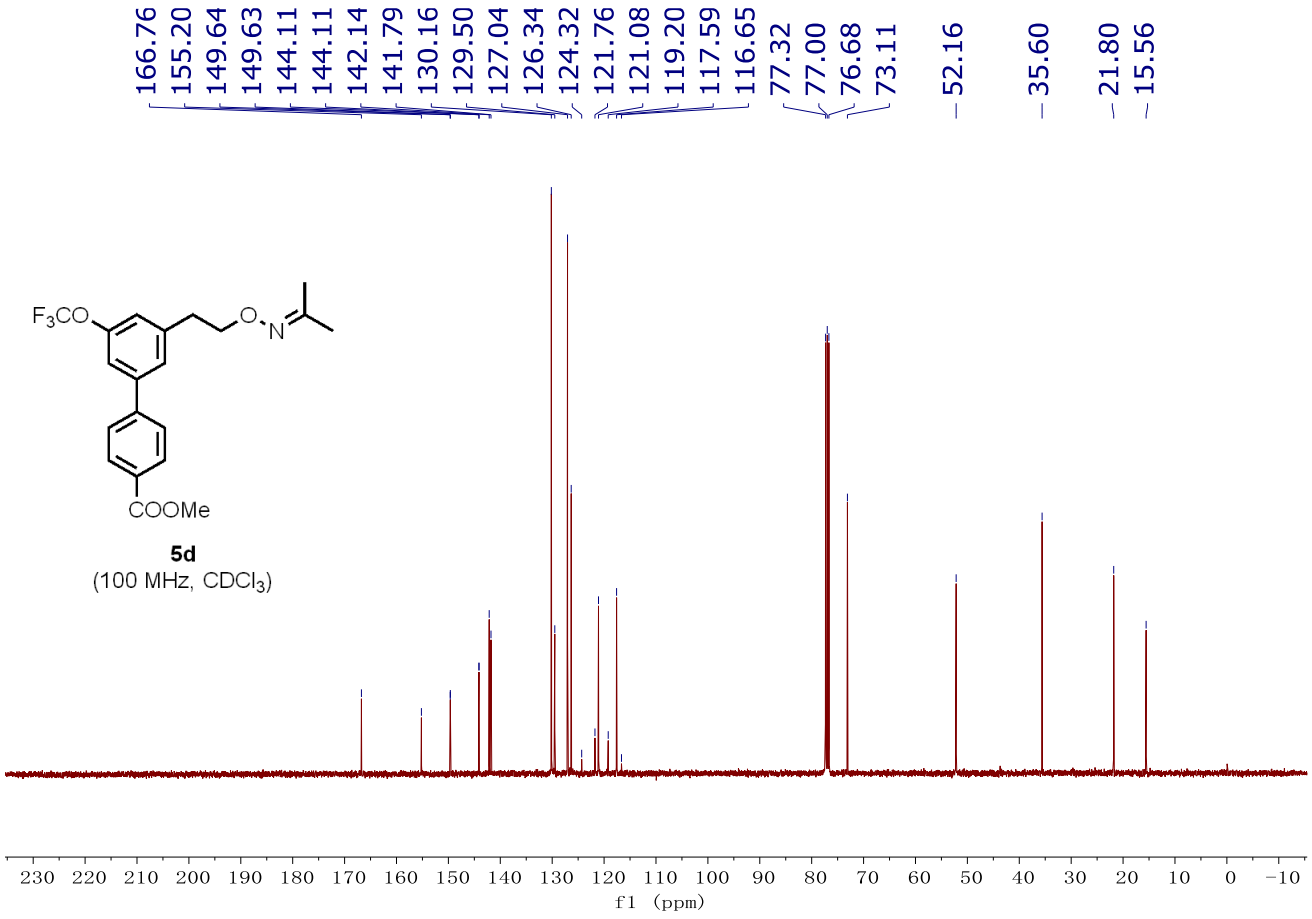


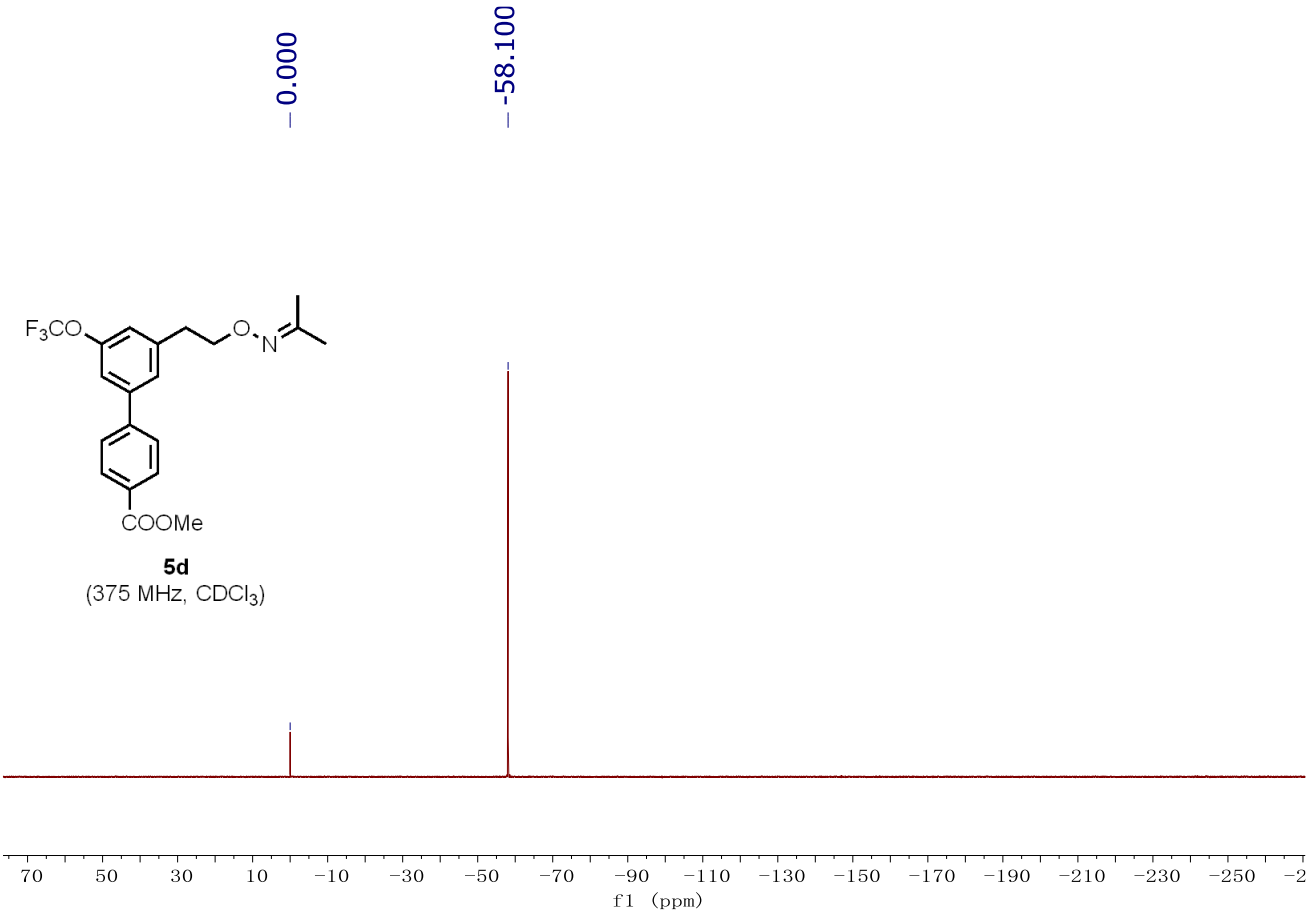
5c
(400 MHz, $CDCl_3$)

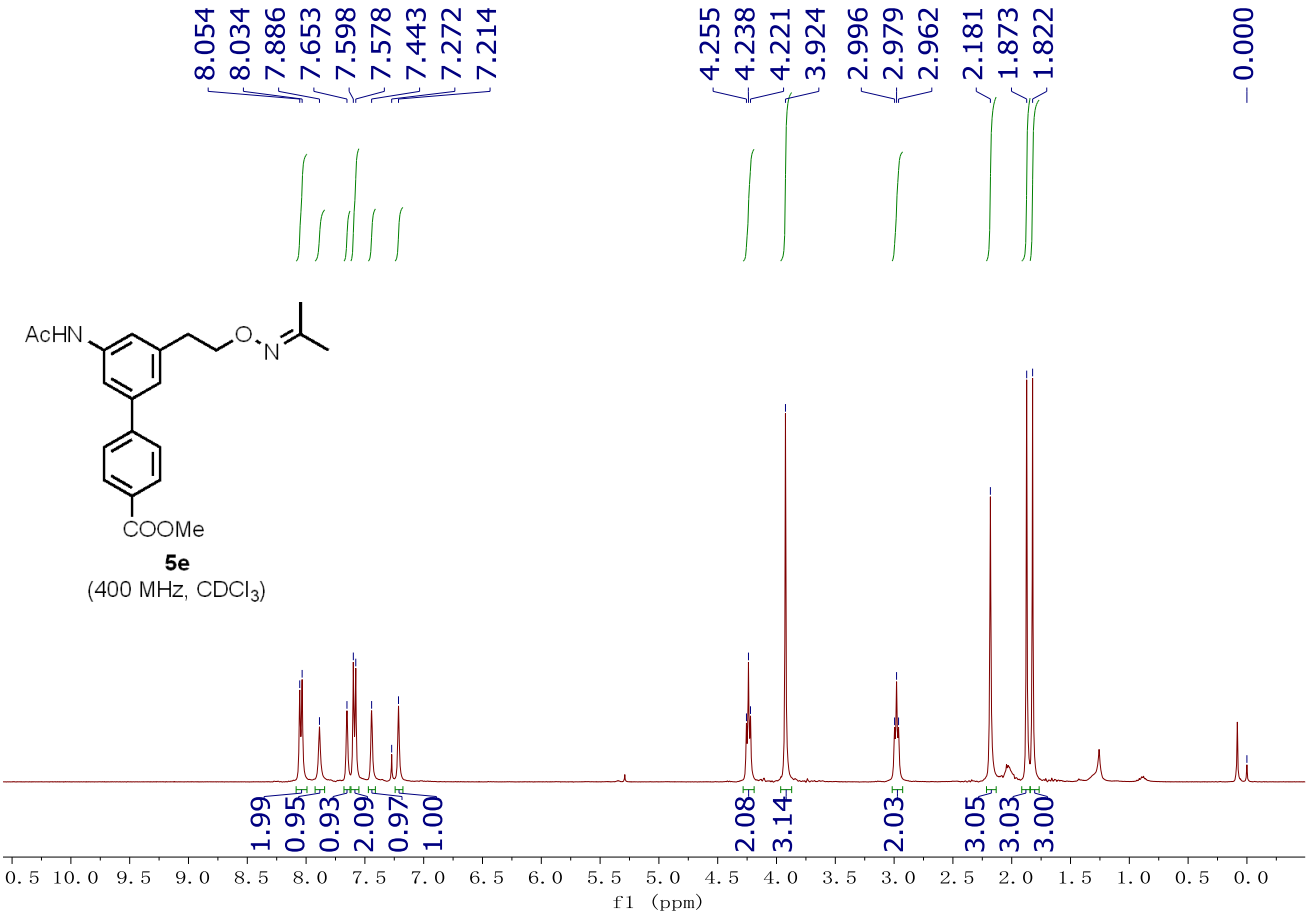


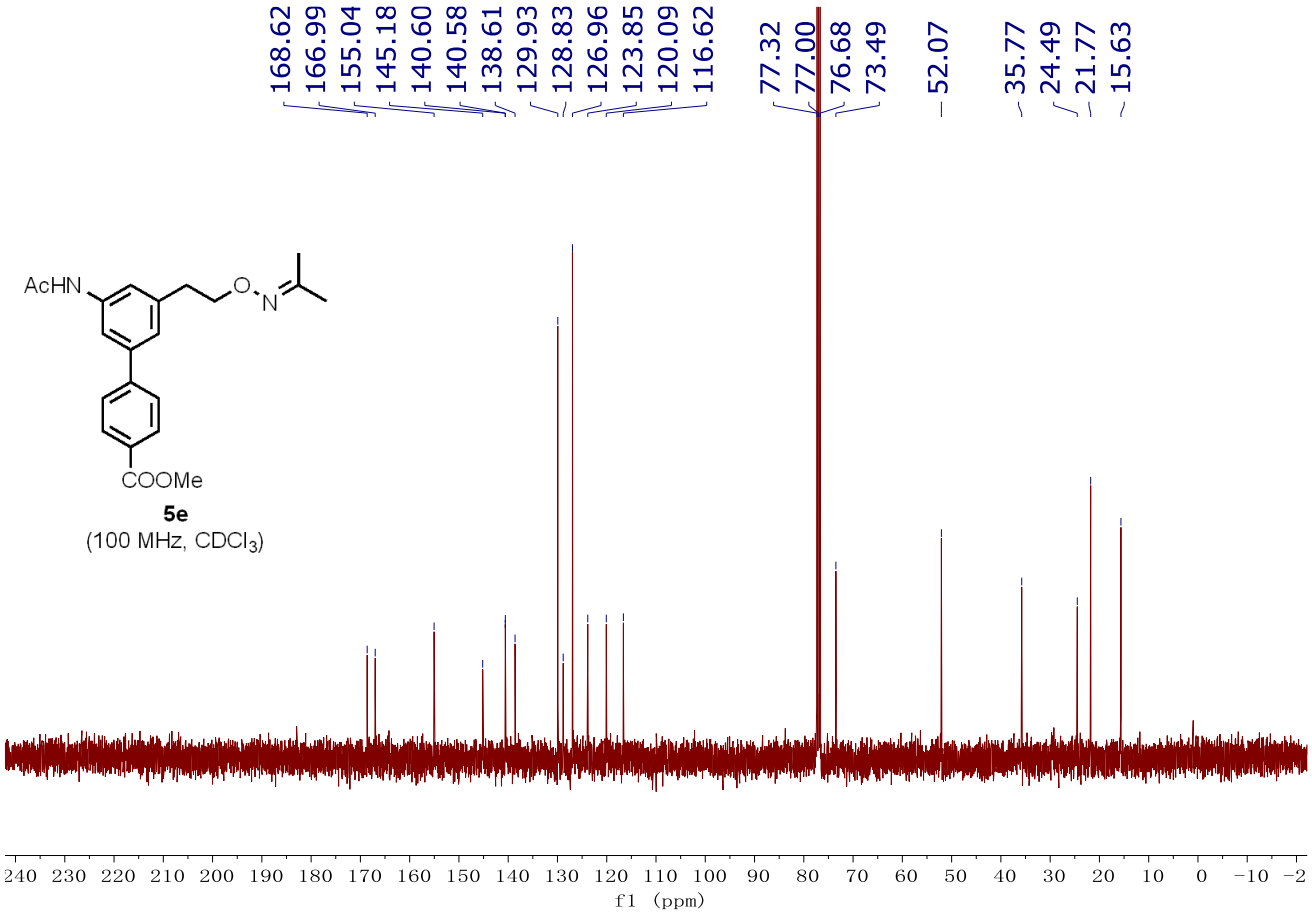
5c
(100 MHz, $CDCl_3$)

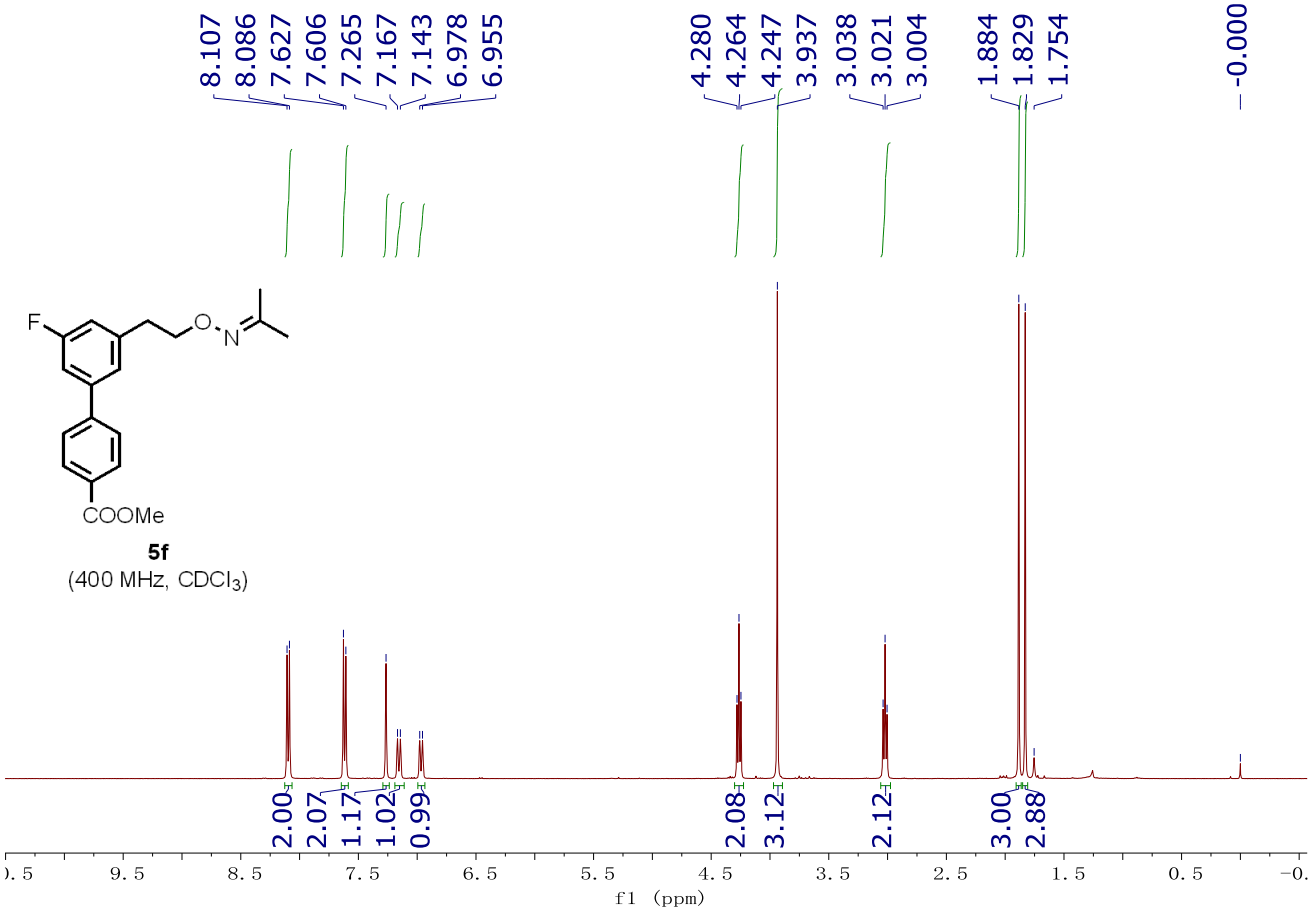

8.124
8.103
7.636
7.616
7.416
7.306
7.265
7.126
4.293
4.276
4.260
3.946
3.065
3.048
3.032
1.886
1.822
1.714
0.000
F3CO
O
N
COOMe
5d
(400 MHz, CDCl3)
2.00
2.05
1.03
1.01
0.99
2.01
3.05
2.04
3.00
2.93
f1 (ppm)

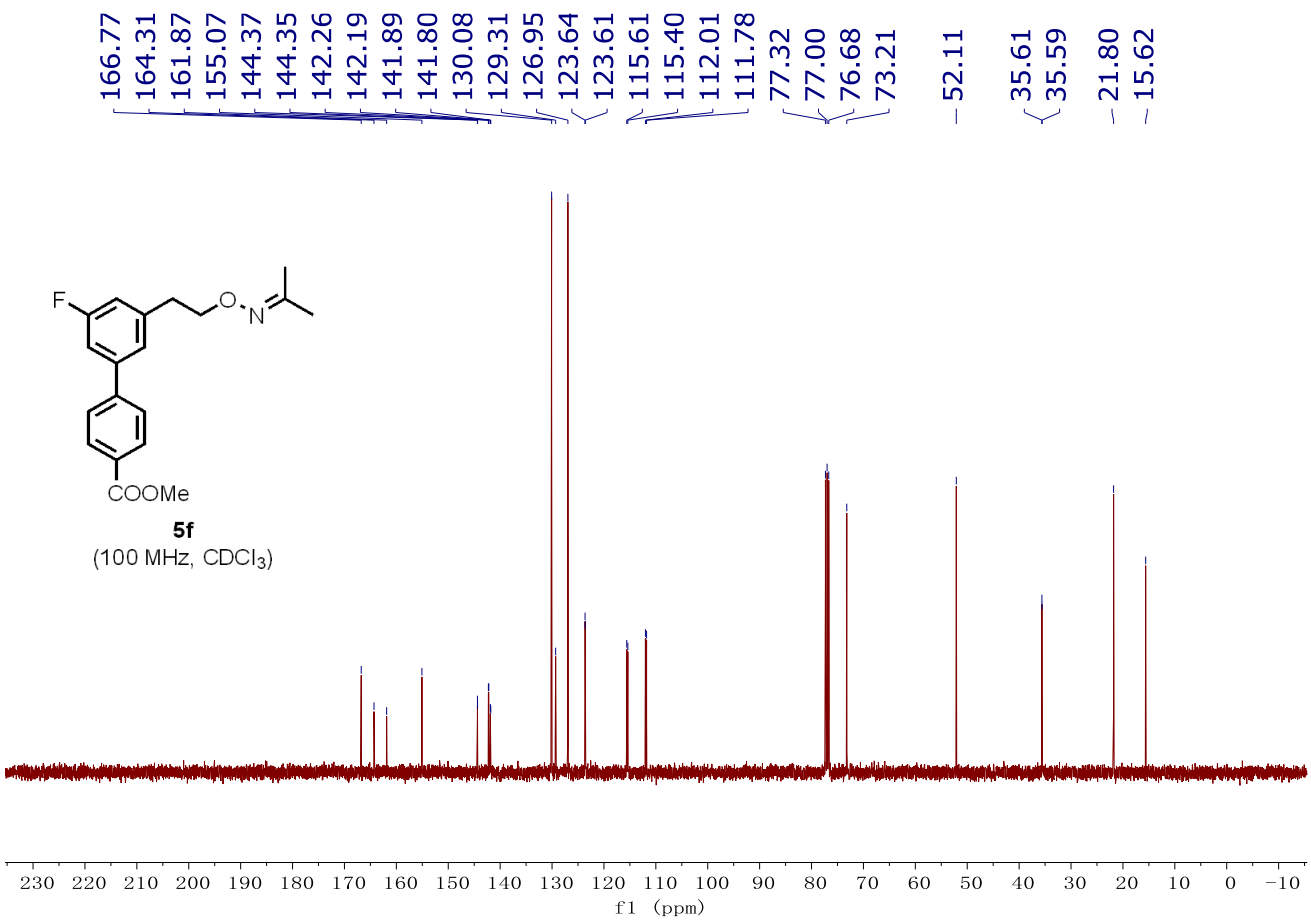

166.76
155.20
149.64
149.63
144.11
144.11
142.14
141.79
130.16
129.50
127.04
126.34
124.32
121.76
121.08
119.20
117.59
116.65
77.32
77.00
76.68
73.11
52.16
35.60
21.80
15.56
F3CO
O
N
COOMe
5d
(100 MHz, CDCl3)
f1 (ppm)

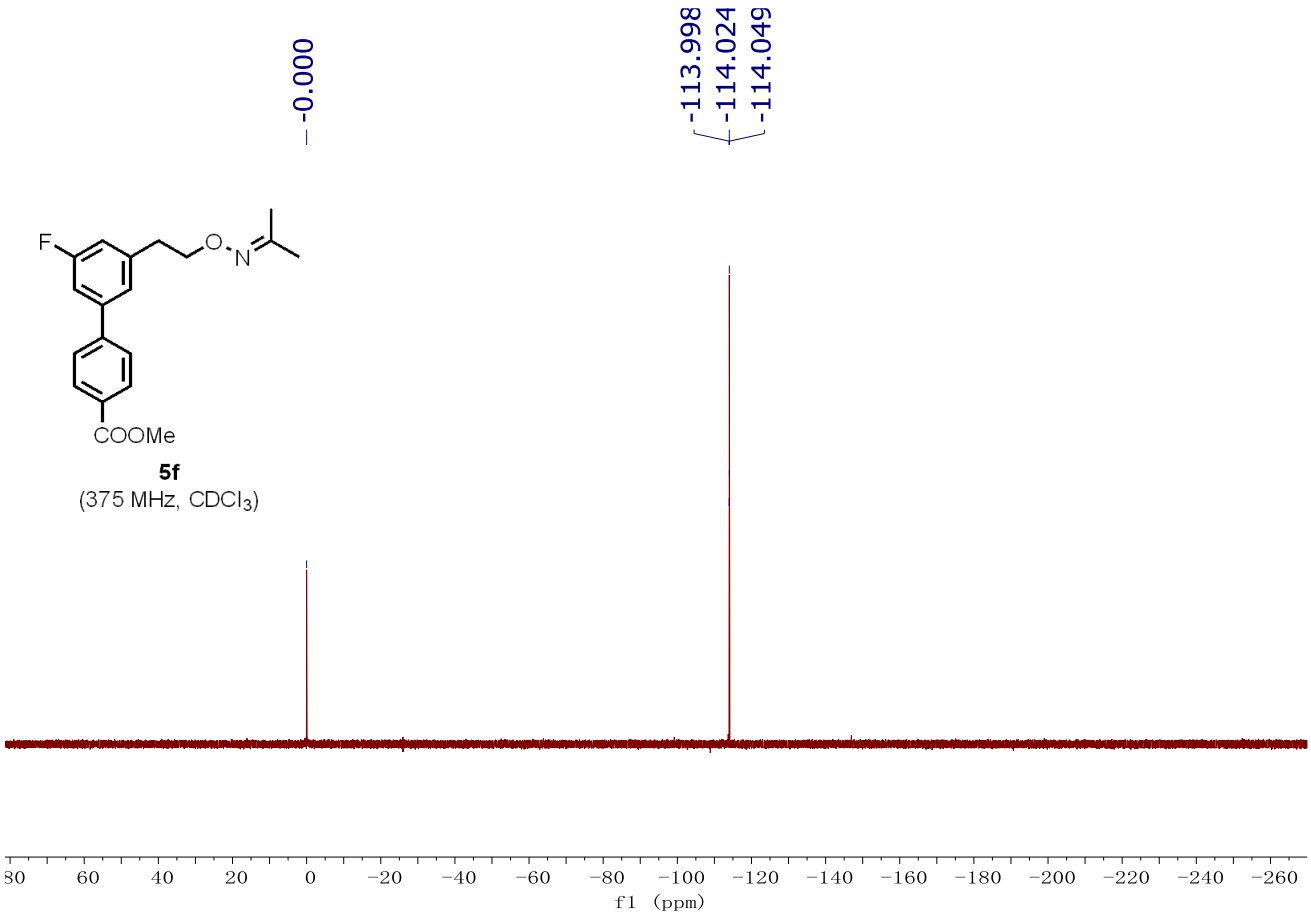

0.000
-58.100
F3CO
O
N
COOMe
5d
(375 MHz, CDCl3)
70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −2
f1 (ppm)

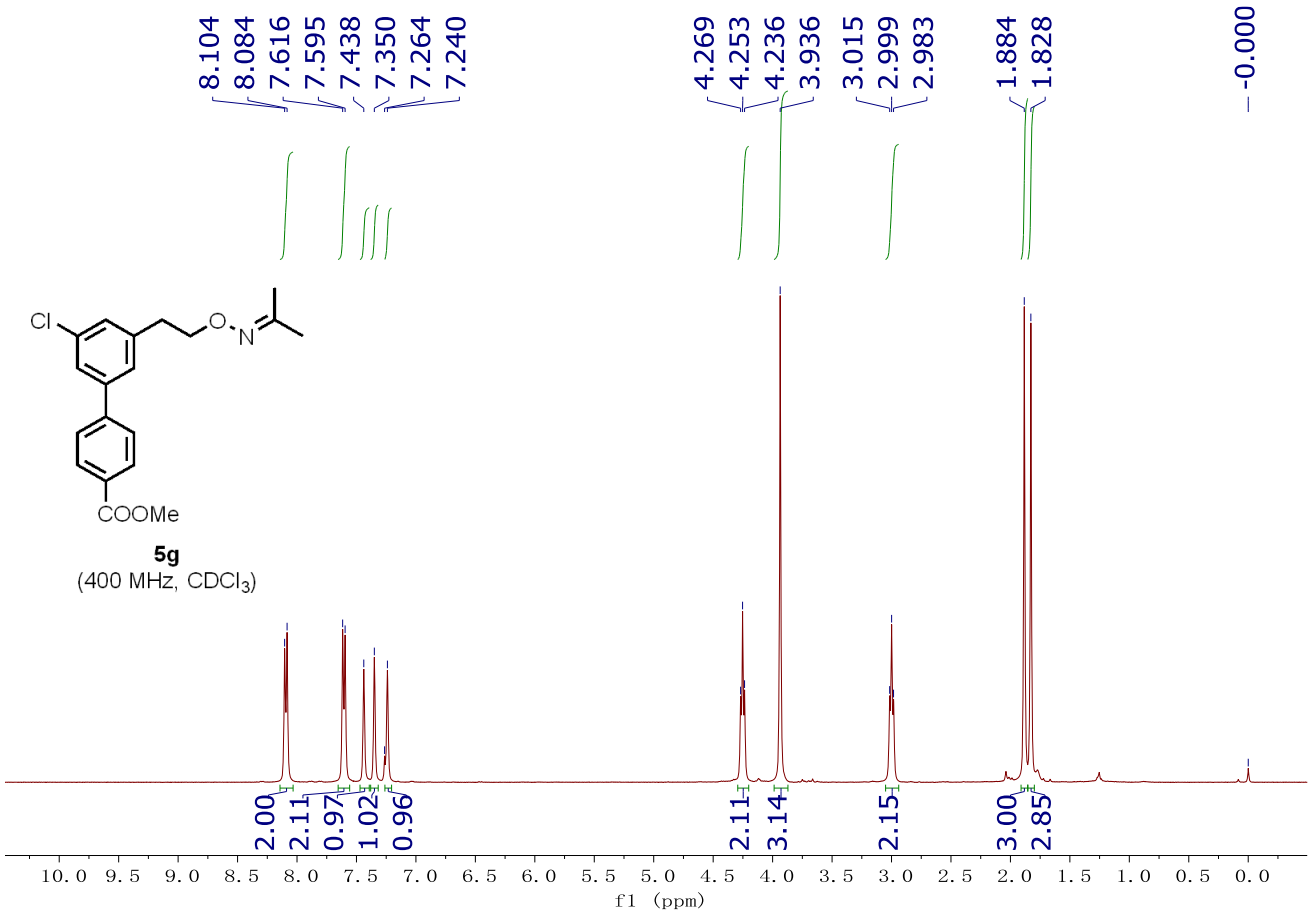

8.054
8.034
7.886
7.653
7.598
7.578
7.443
7.272
7.214
4.255
4.238
4.221
3.924
2.996
2.979
2.962
2.181
1.873
1.822
0.000
AcHN
O
N
COOMe
5e
(400 MHz, CDCl3)
1.99
0.95
0.93
2.09
0.97
1.00
2.08
3.14
2.03
3.05
3.03
3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

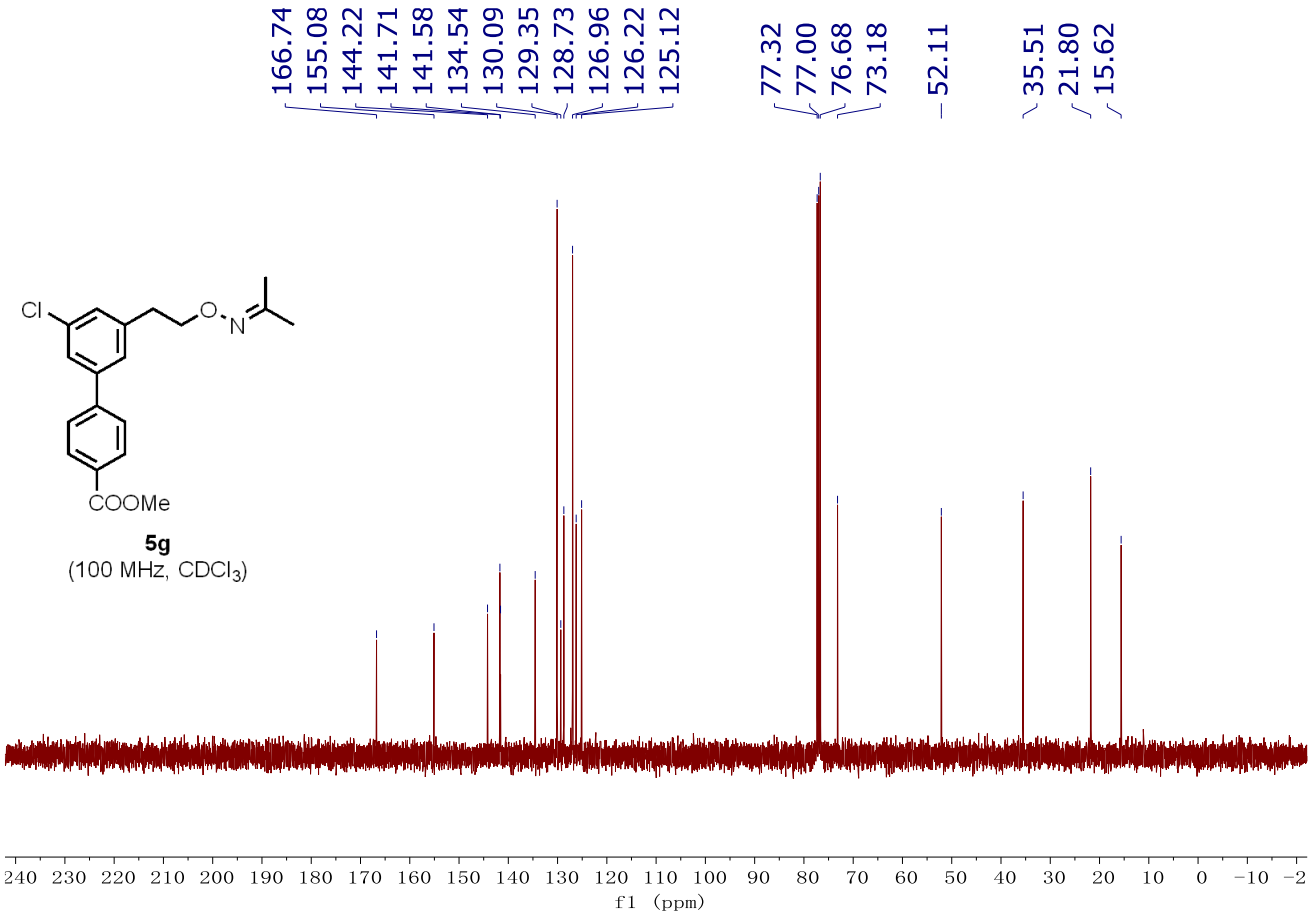

168.62
166.99
155.04
145.18
140.60
140.58
138.61
129.93
128.83
126.96
123.85
120.09
116.62
77.32
77.00
76.68
73.49
52.07
35.77
24.49
21.77
15.63
AcHN
O
N
COOMe
5e
(100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −2
f1 (ppm)

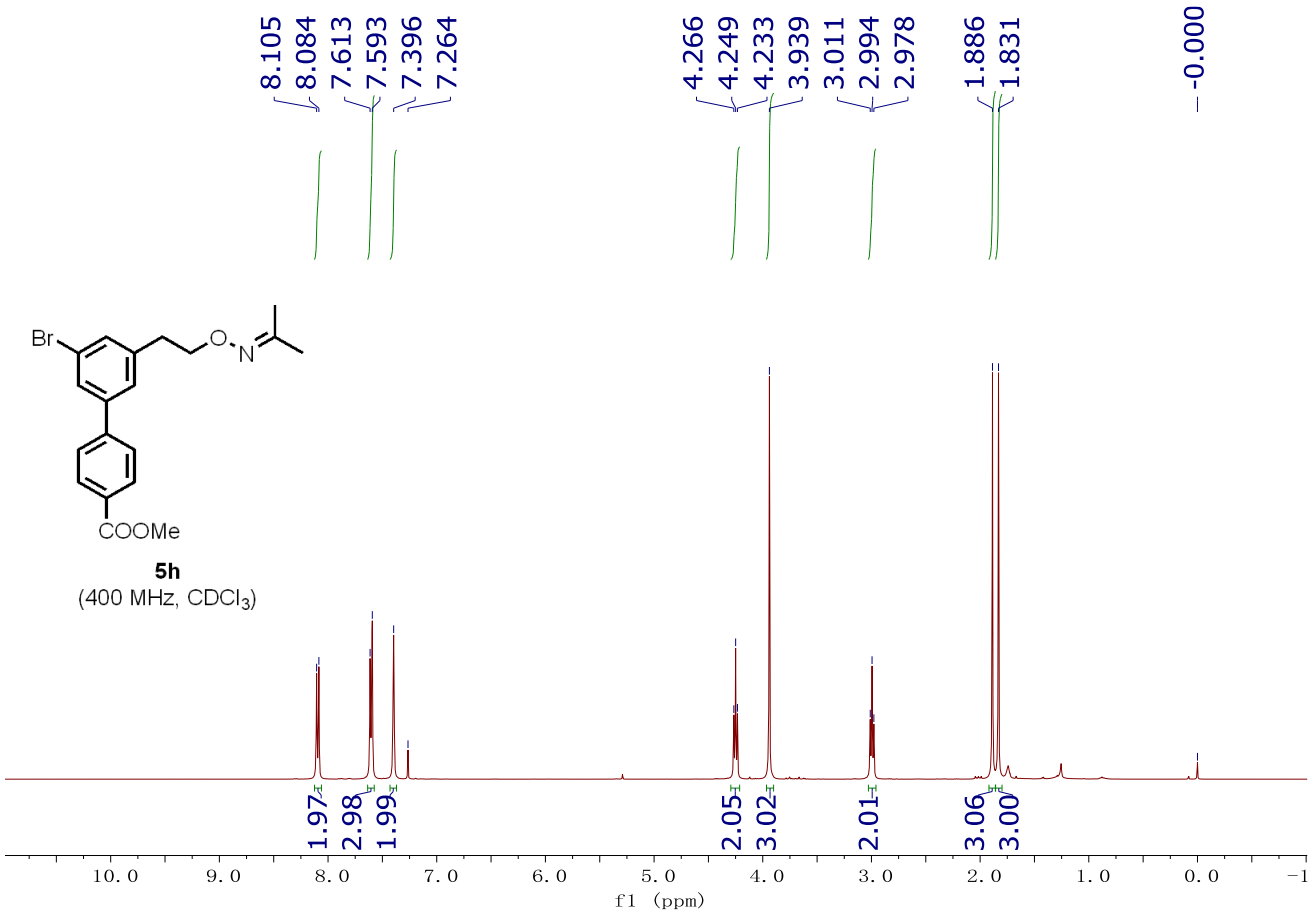

8.107
8.086
7.627
7.606
7.265
7.167
7.143
6.978
6.955
4.280
4.264
4.247
3.937
3.038
3.021
3.004
1.884
1.829
1.754
-0.000
F
O
N
COOMe
5f
(400 MHz, CDCl3)
2.00
2.07
1.17
1.02
0.99
2.08
3.12
2.12
3.00
2.88
f1 (ppm)

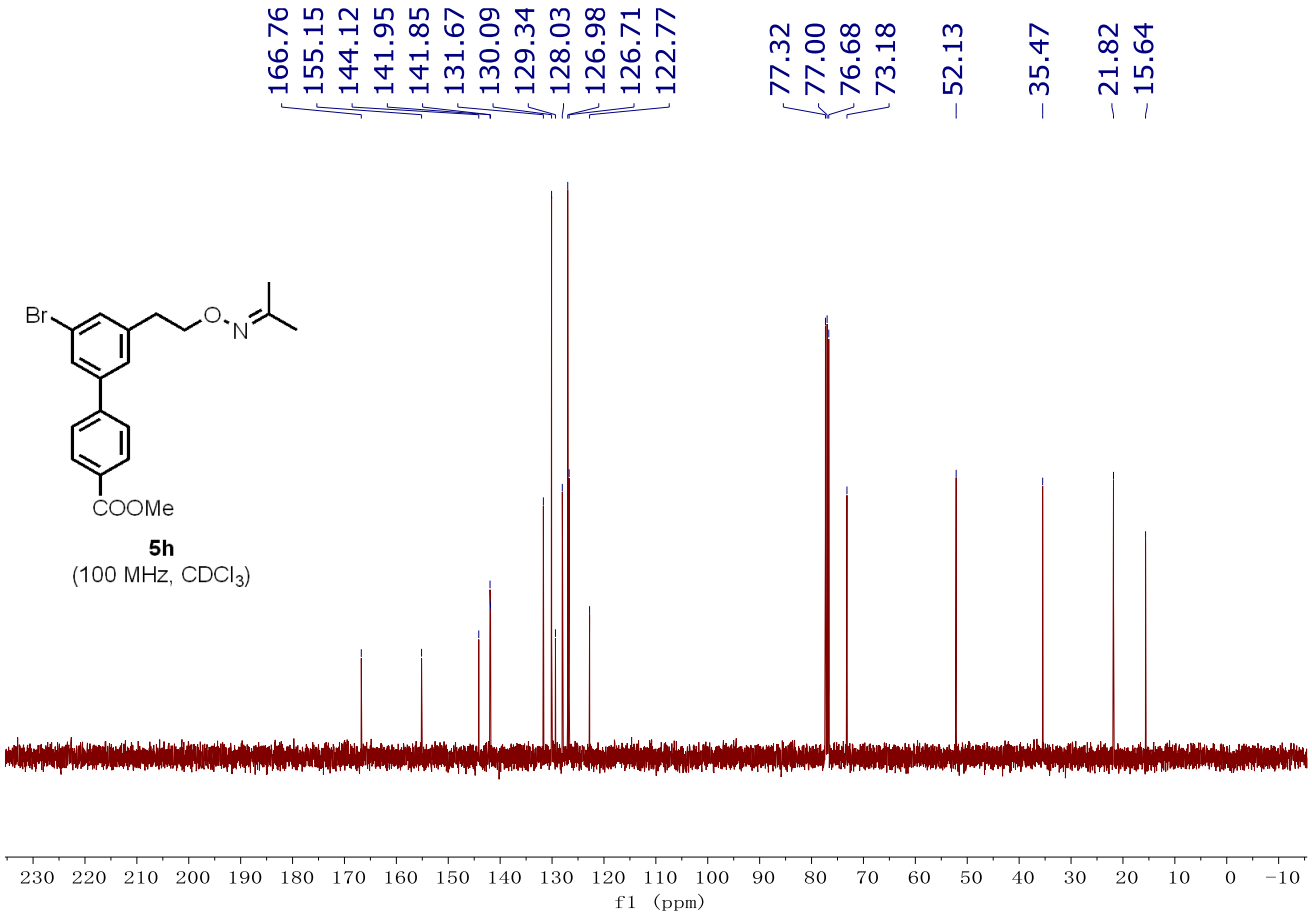

166.77
164.31
161.87
155.07
144.37
144.35
142.26
142.19
141.89
141.80
130.08
129.31
126.95
123.64
123.61
115.61
115.40
112.01
111.78
77.32
77.00
76.68
73.21
52.11
35.61
35.59
21.80
15.62
F
O
N
COOMe
5f
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

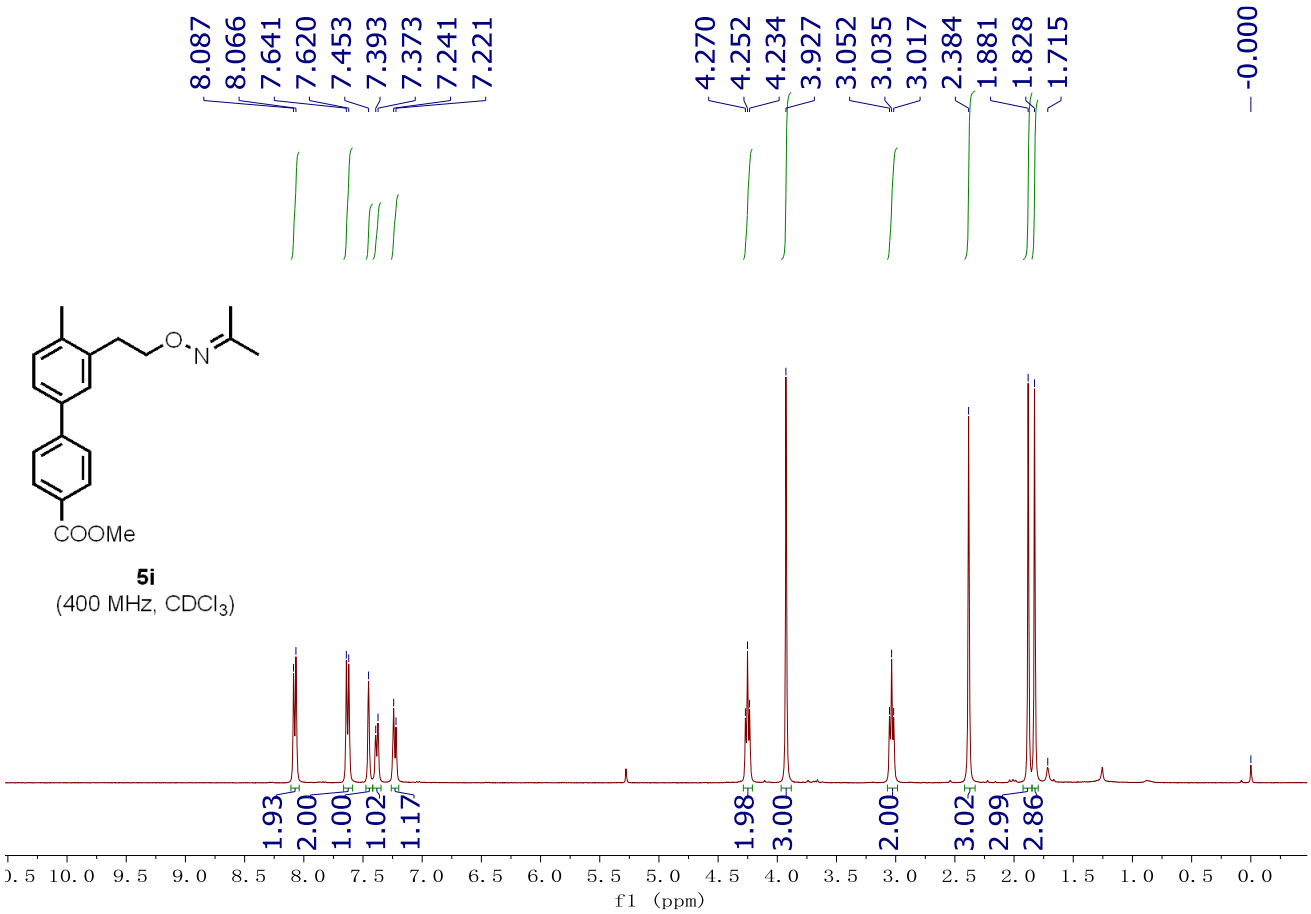

-0.000
-113.998
-114.024
-114.049
F
O
N
COOMe
5f
(375 MHz, CDCl3)
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260
f1 (ppm)


8.104
8.084
7.616
7.595
7.438
7.350
7.264
7.240
4.269
4.253
4.236
3.936
3.015
2.999
2.983
1.884
1.828
-0.000
Cl
O
N
COOMe
5g
(400 MHz, CDCl3)
2.00
2.11
0.97
1.02
0.96
2.11
3.14
2.15
3.00
2.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

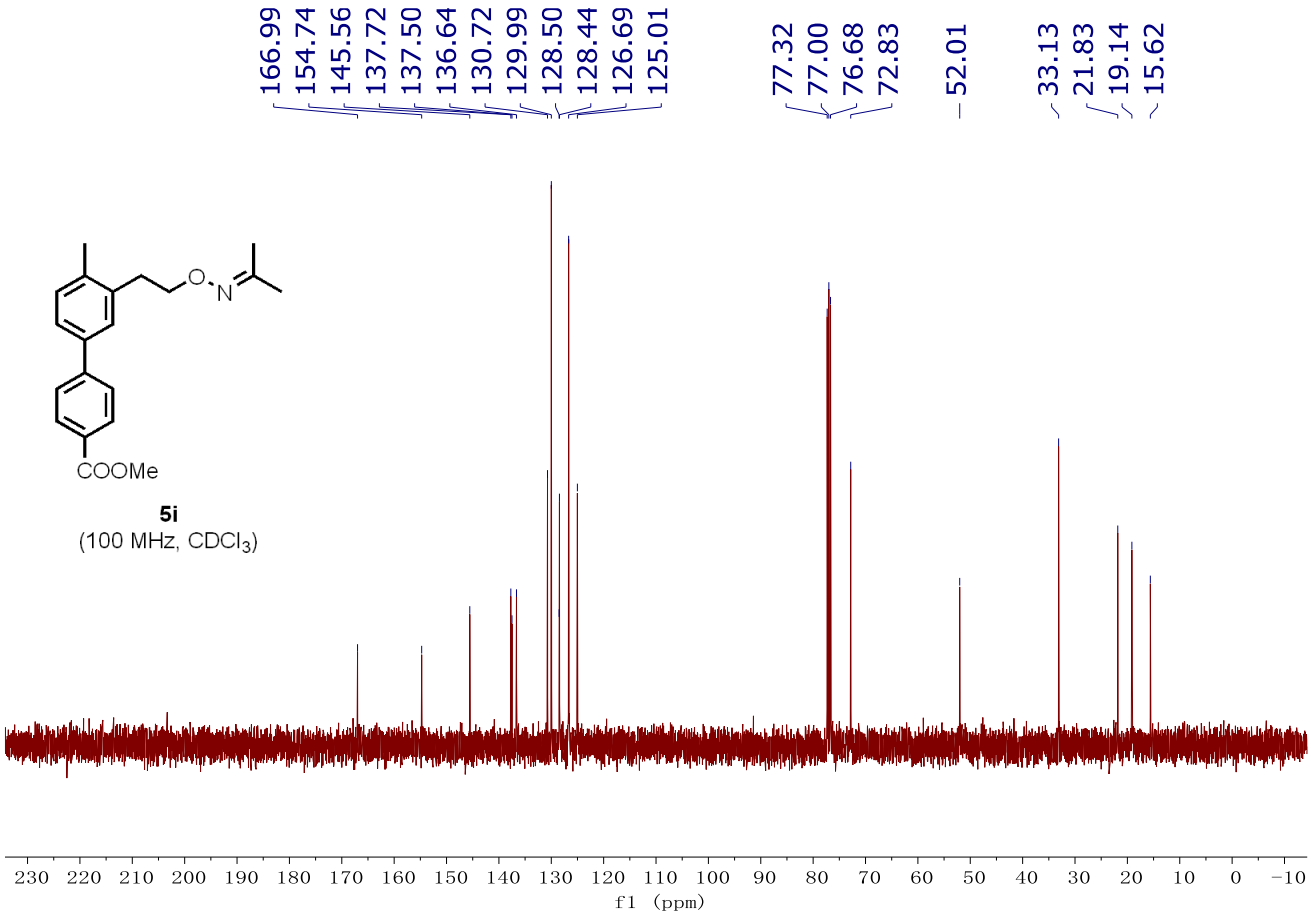

166.74
155.08
144.22
141.71
141.58
134.54
130.09
129.35
128.73
126.96
126.22
125.12
77.32
77.00
76.68
73.18
52.11
35.51
21.80
15.62
Cl
O
N
COOMe
5g
(100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


8.105
8.084
7.613
7.593
7.396
7.264
4.266
4.249
4.233
3.939
3.011
2.994
2.978
1.886
1.831
-0.000
Br
O
N
COOMe
5h
(400 MHz, CDCl3)
1.97
2.98
1.99
2.05
3.02
2.01
3.06
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

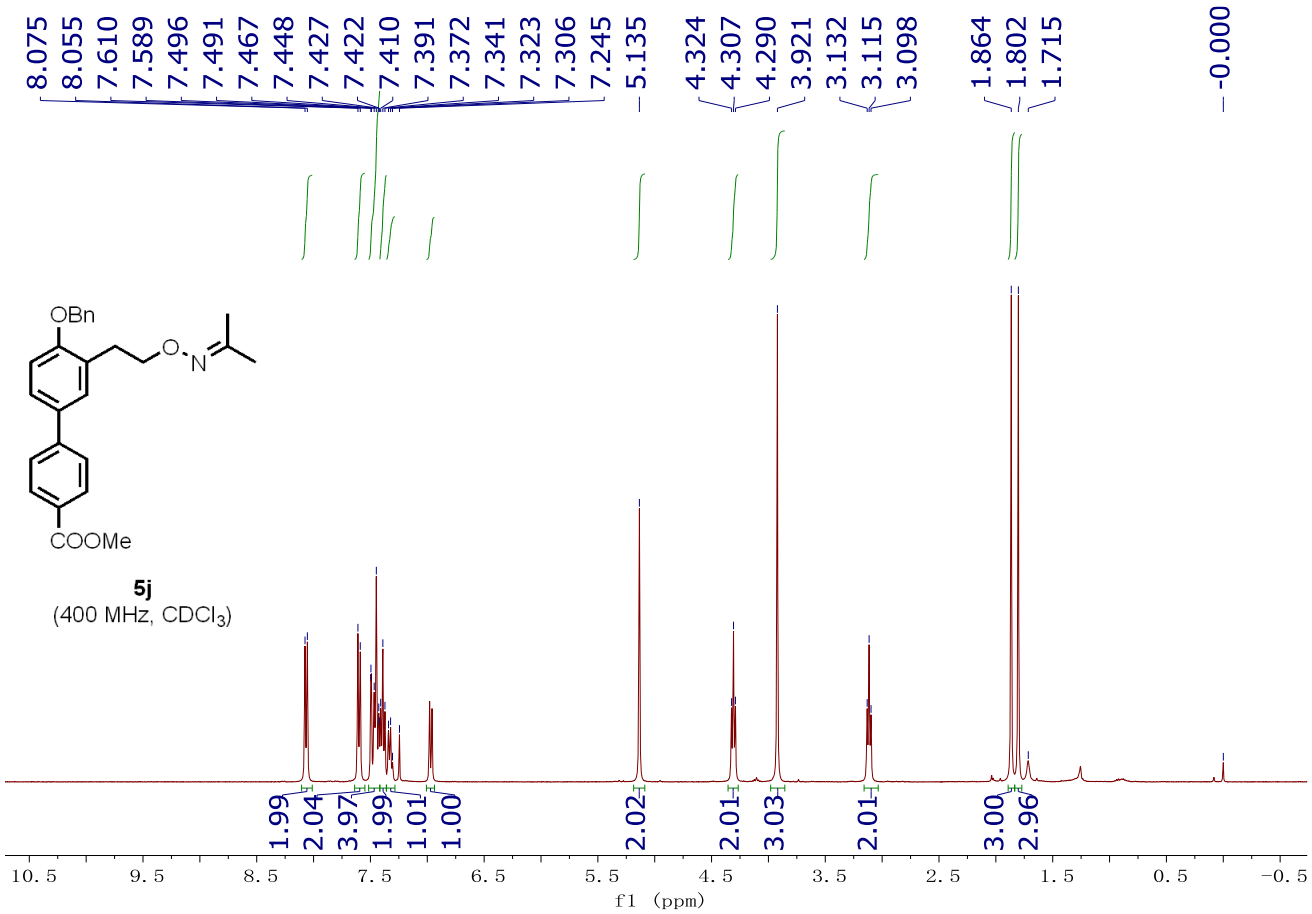

166.76
155.15
144.12
141.95
141.85
131.67
130.09
129.34
128.03
126.98
126.71
122.77
77.32
77.00
76.68
73.18
52.13
35.47
21.82
15.64
Br
O
N
COOMe
5h
(100 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

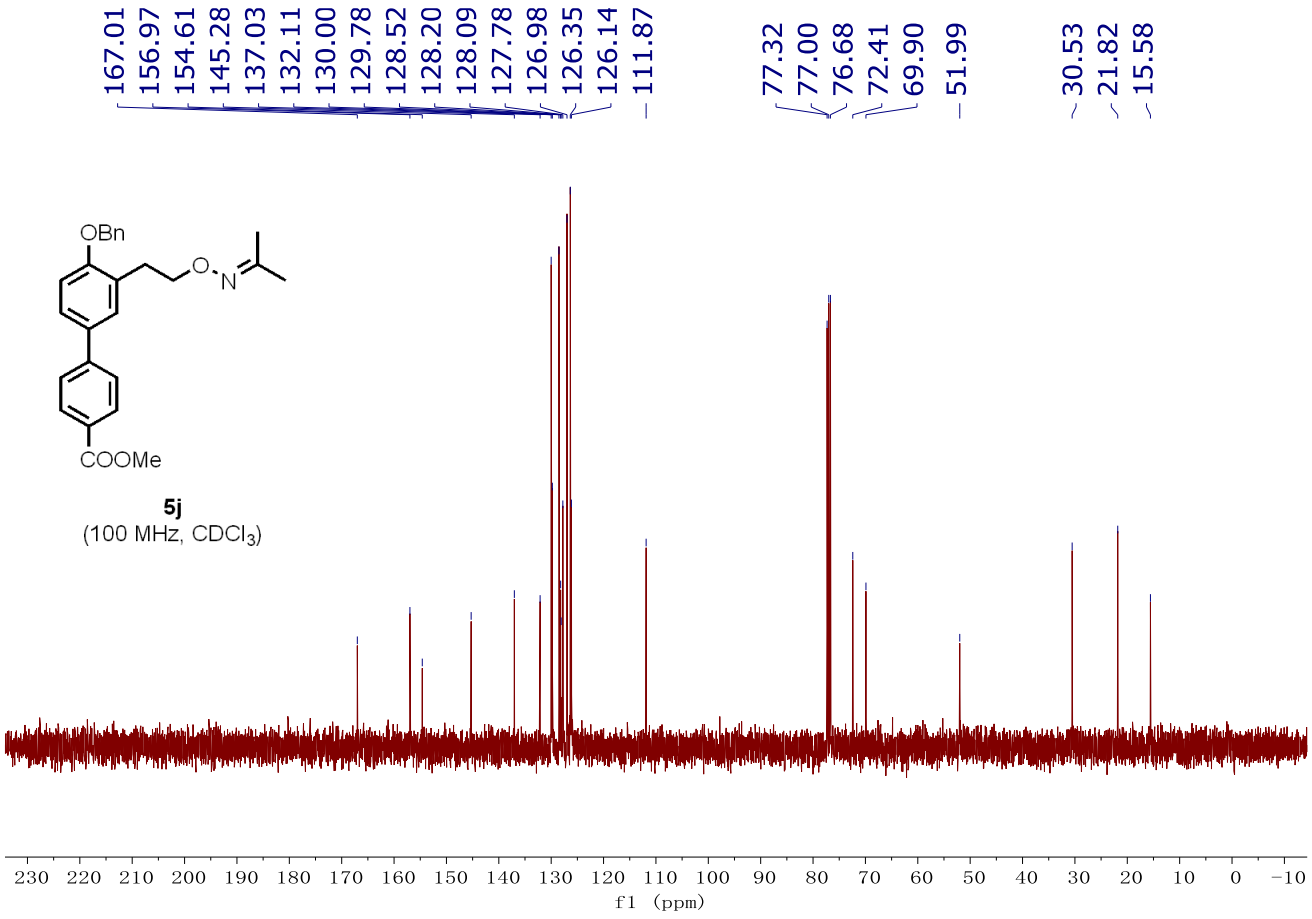


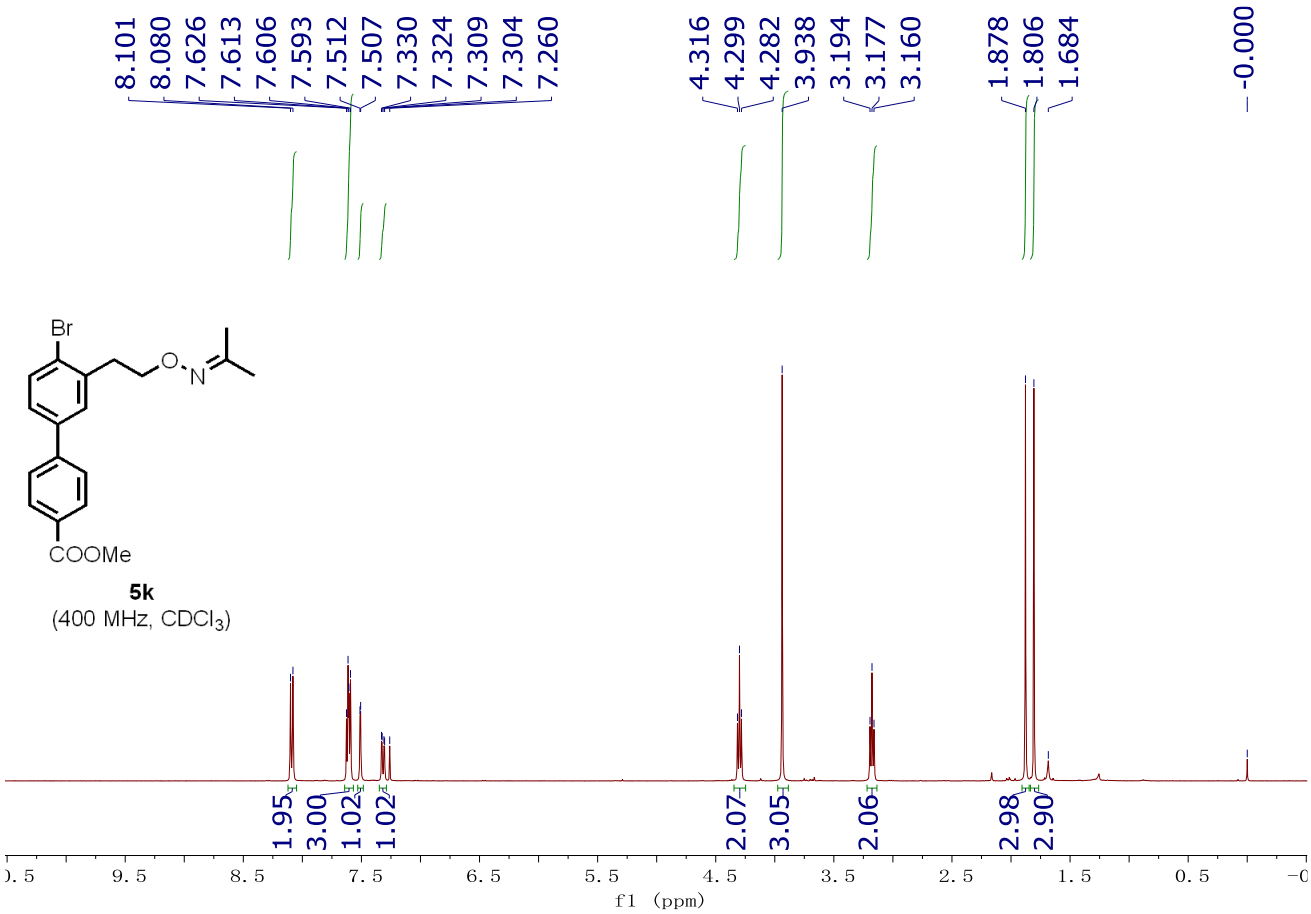
5i
(400 MHz, $CDCl_3$)

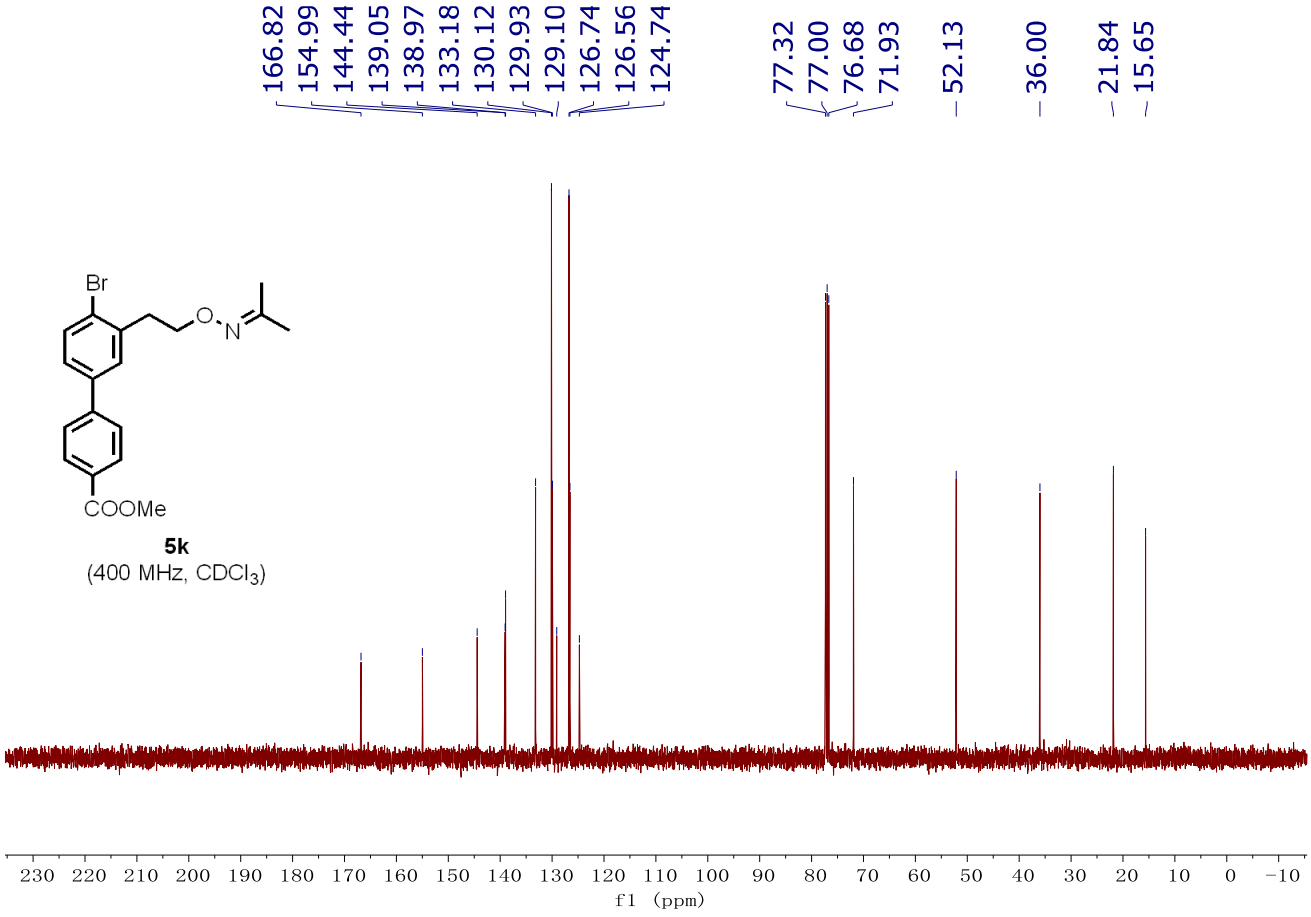


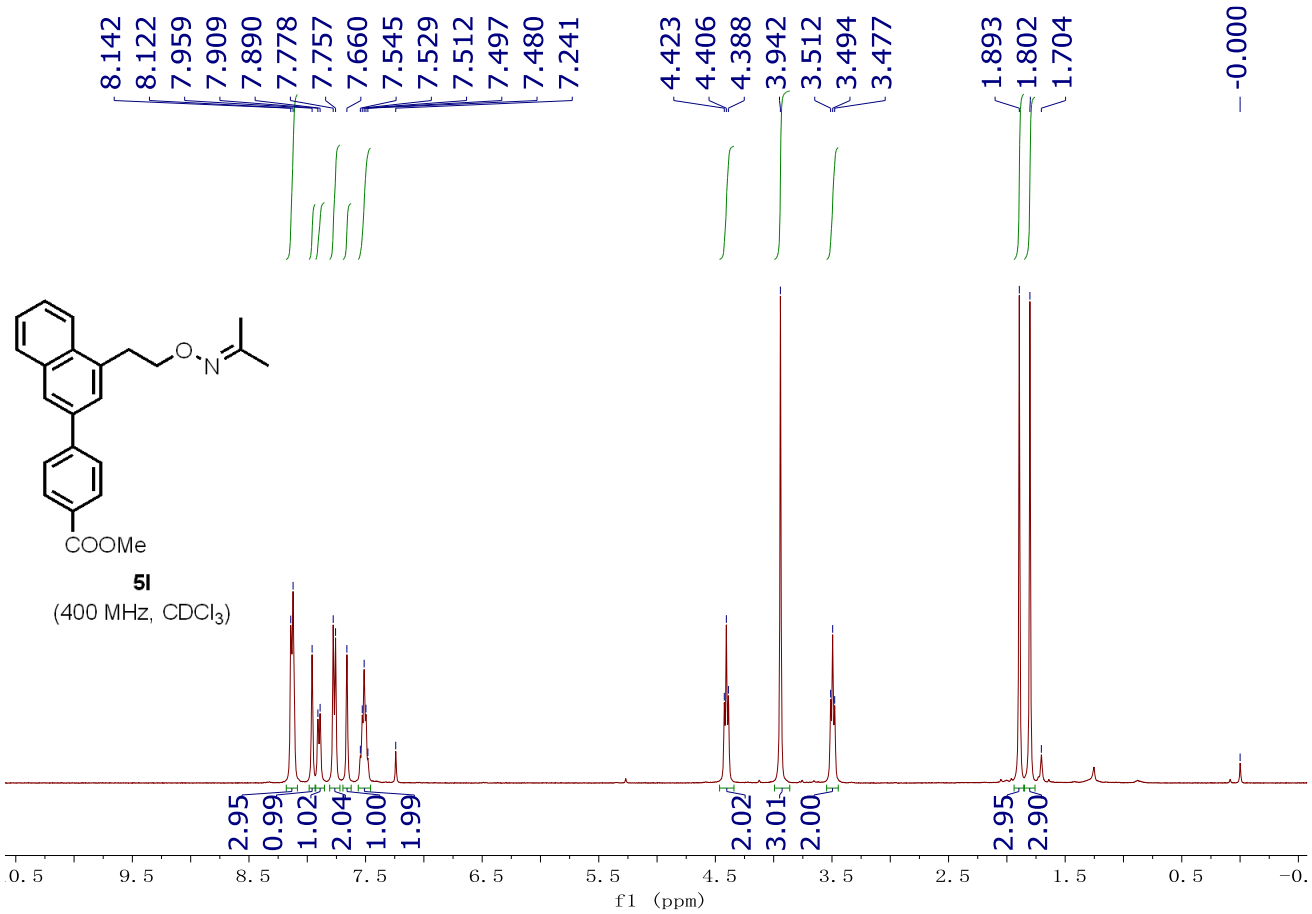
5i
(100 MHz, $CDCl_3$)

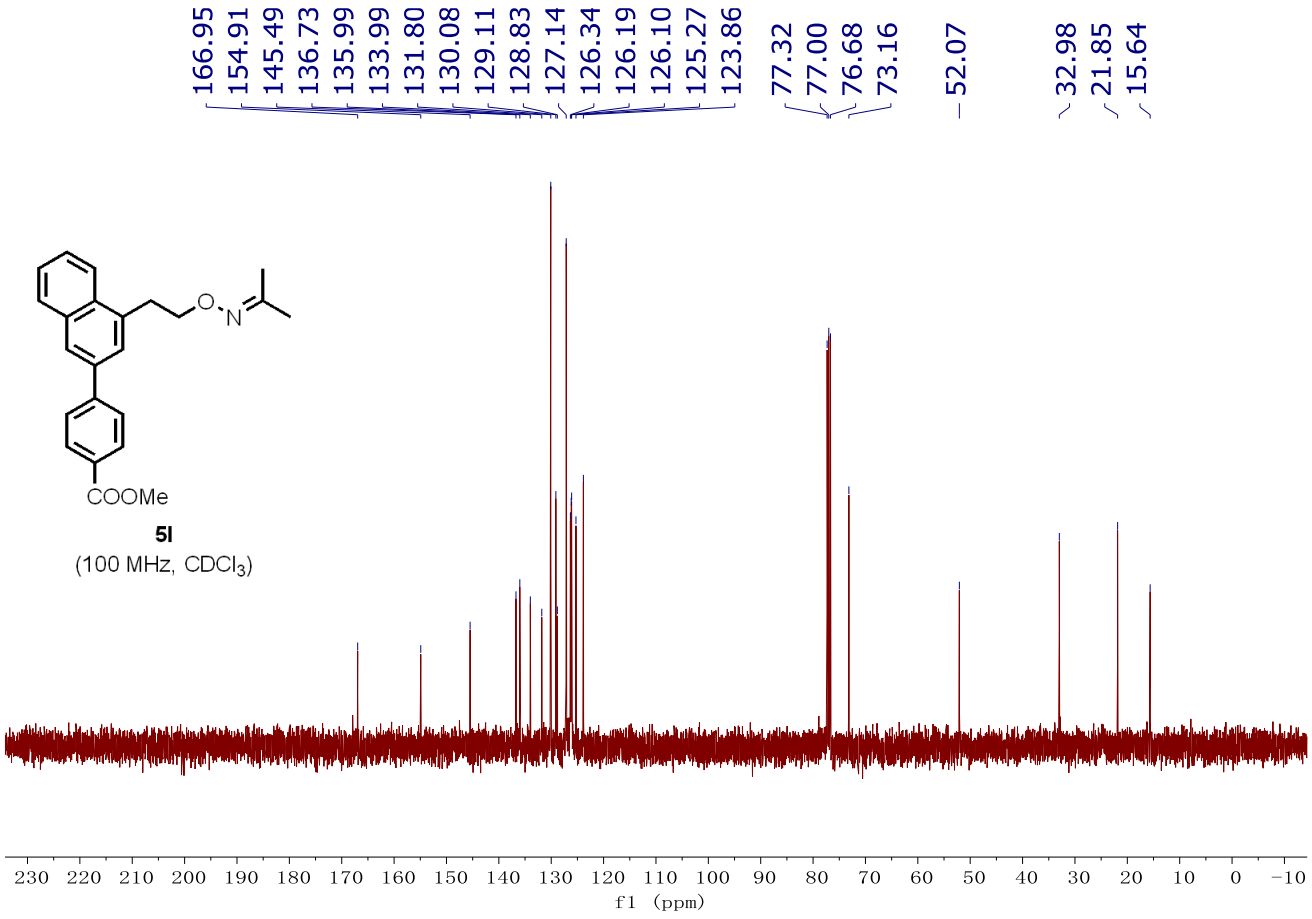

8.075
8.055
7.610
7.589
7.496
7.491
7.467
7.448
7.427
7.422
7.410
7.391
7.372
7.341
7.323
7.306
7.245
5.135
4.324
4.307
4.290
3.921
3.132
3.115
3.098
1.864
1.802
1.715
-0.000
OBn
O
N
COOMe
5j
(400 MHz, CDCl3)
1.99
2.04
3.97
1.99
1.01
1.00
2.02
2.01
3.03
2.01
3.00
2.96
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

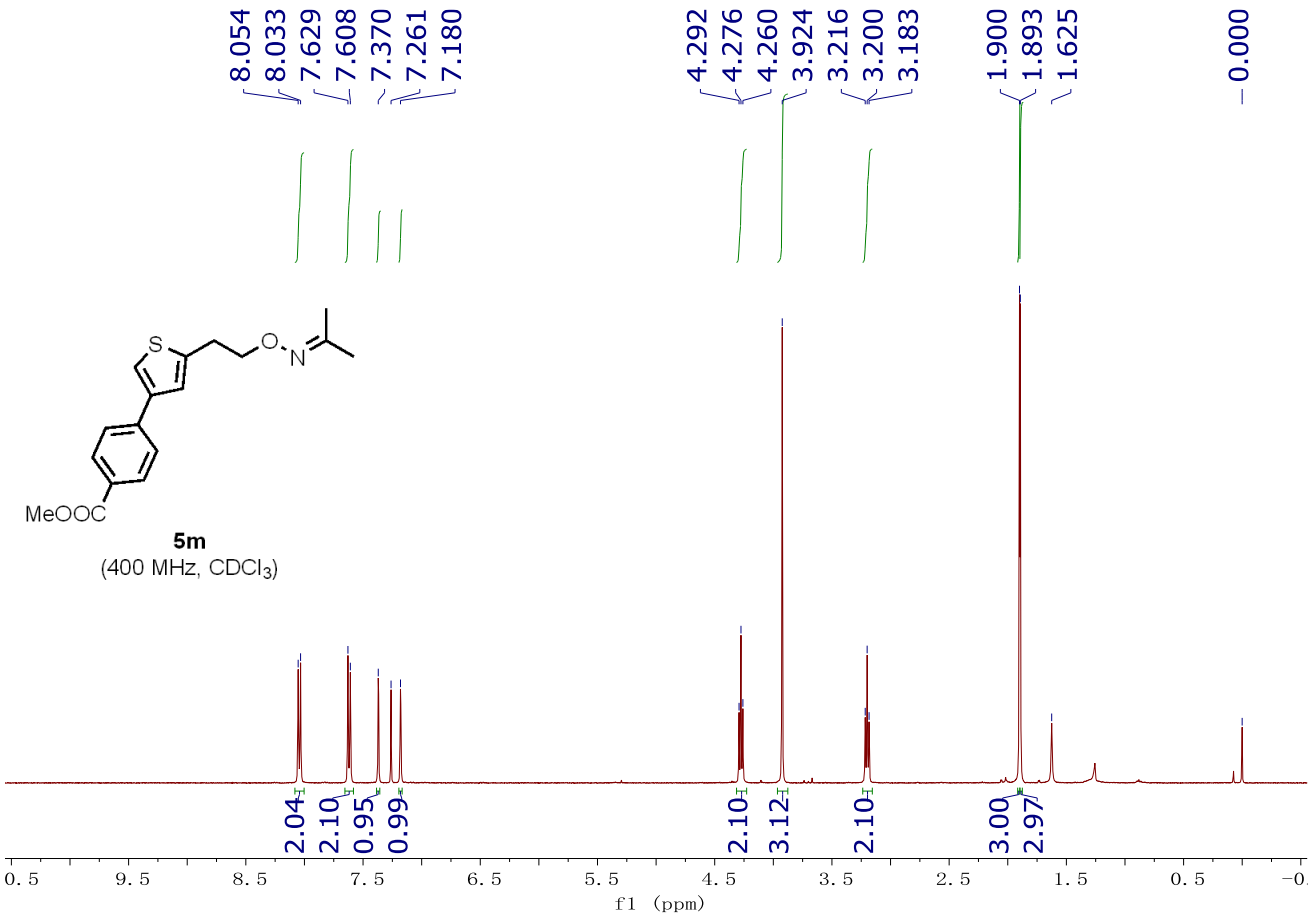

167.01
156.97
154.61
145.28
137.03
132.11
130.00
129.78
128.52
128.20
128.09
127.78
126.98
126.35
126.14
111.87
77.32
77.00
76.68
72.41
69.90
51.99
30.53
21.82
15.58
OBn
O
N
COOMe
5j
(100 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

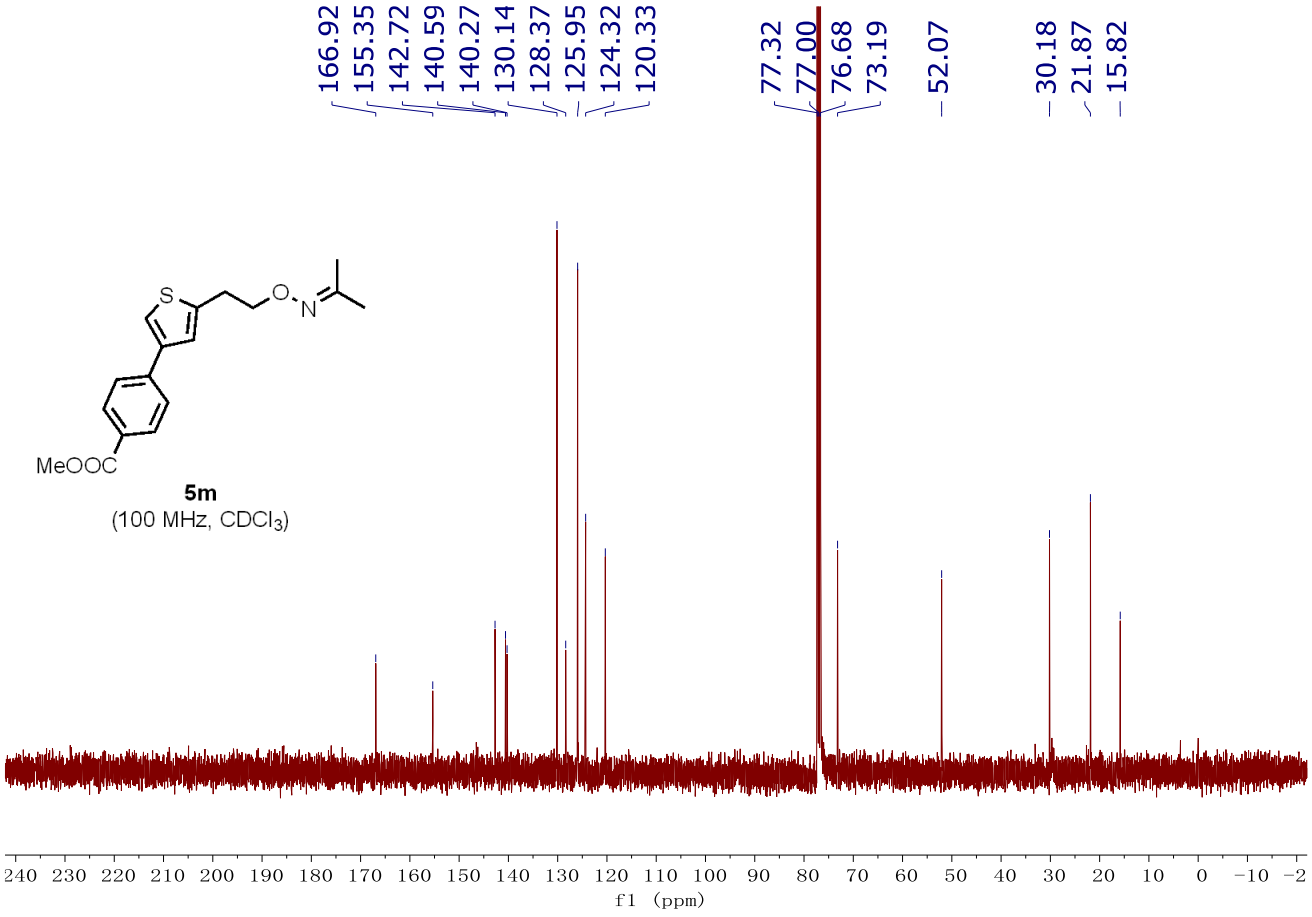

8.101
8.080
7.626
7.613
7.606
7.593
7.512
7.507
7.330
7.324
7.309
7.304
7.260
4.316
4.299
4.282
3.938
3.194
3.177
3.160
1.878
1.806
1.684
-0.000
Br
O
N
COOMe
5k
(400 MHz, CDCl3)
1.95
3.00
1.02
1.02
2.07
3.05
2.06
2.98
2.90
f1 (ppm)

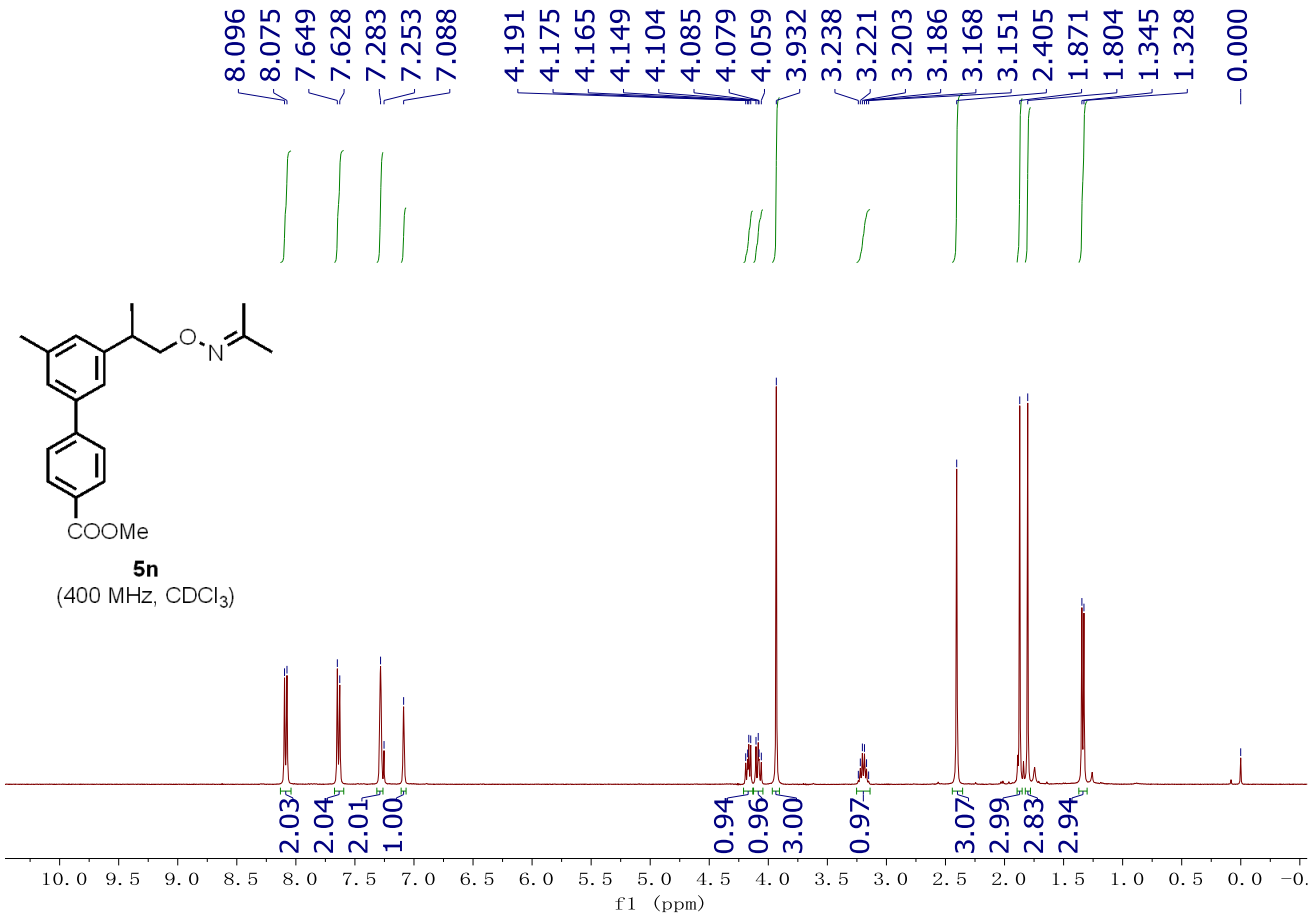

166.82
154.99
144.44
139.05
138.97
133.18
130.12
129.93
129.10
126.74
126.56
124.74
77.32
77.00
76.68
71.93
52.13
36.00
21.84
15.65
Br
O
N
COOMe
5k
(400 MHz, CDCl3)
f1 (ppm)

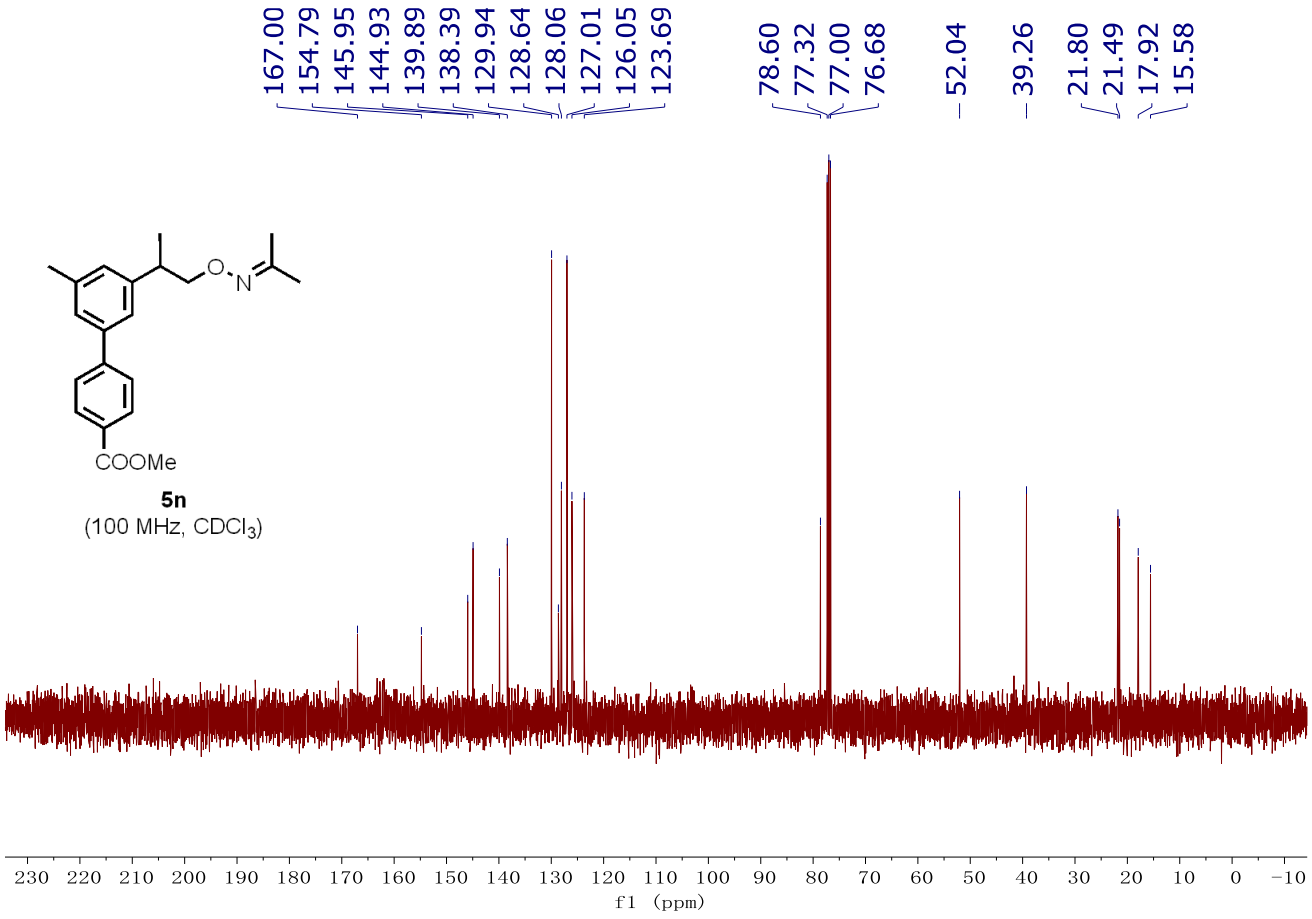

8.142
8.122
7.959
7.909
7.890
7.778
7.757
7.660
7.545
7.529
7.512
7.497
7.480
7.241
4.423
4.406
4.388
3.942
3.512
3.494
3.477
1.893
1.802
1.704
-0.000
COOMe
5l
(400 MHz, CDCl3)
2.95
0.99
1.02
2.04
1.00
1.99
2.02
3.01
2.00
2.95
2.90
f1 (ppm)

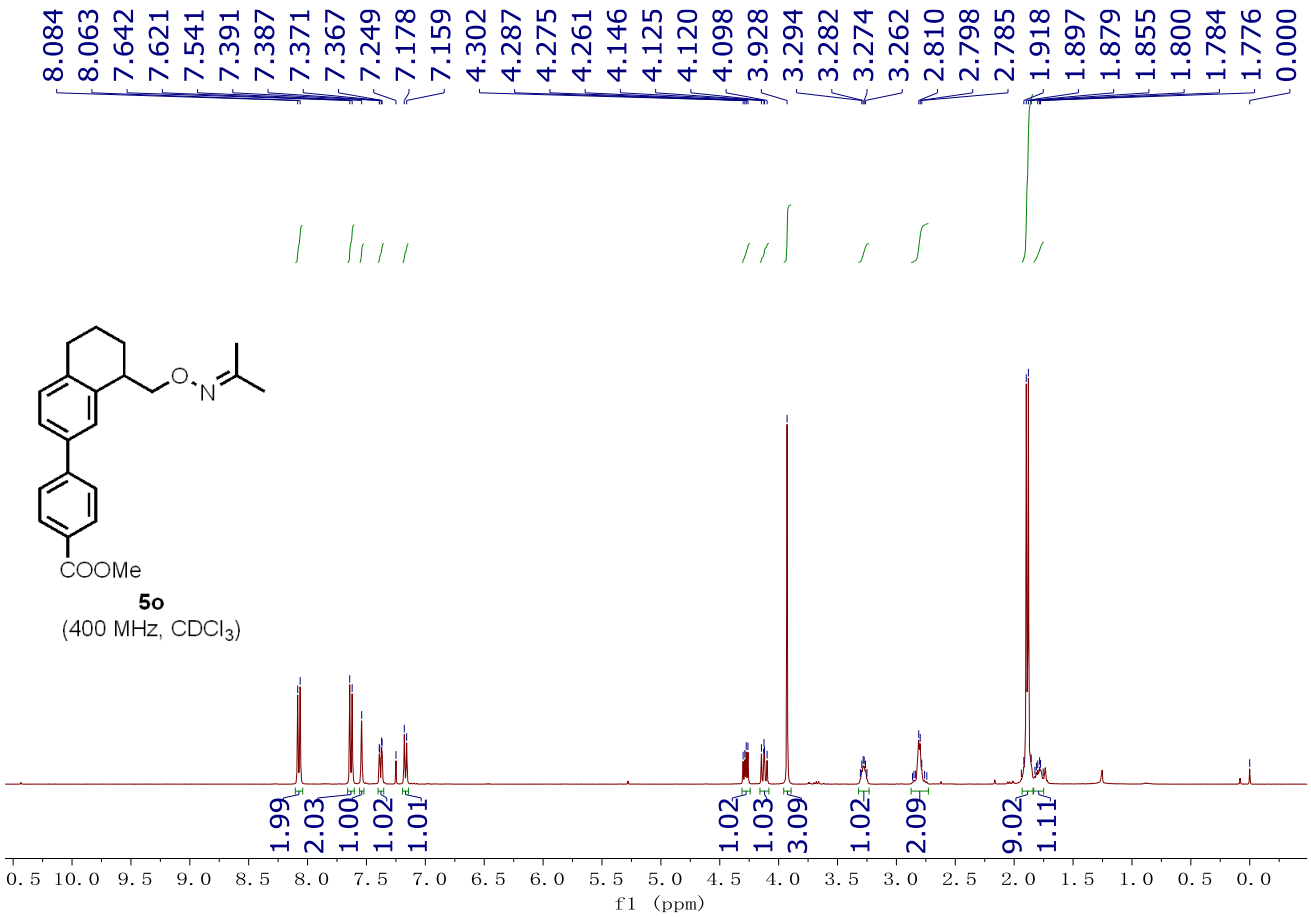

166.95
154.91
145.49
136.73
135.99
133.99
131.80
130.08
129.11
128.83
127.14
126.34
126.19
126.10
125.27
123.86
77.32
77.00
76.68
73.16
52.07
32.98
21.85
15.64
COOMe
5l
(100 MHz, CDCl3)
f1 (ppm)

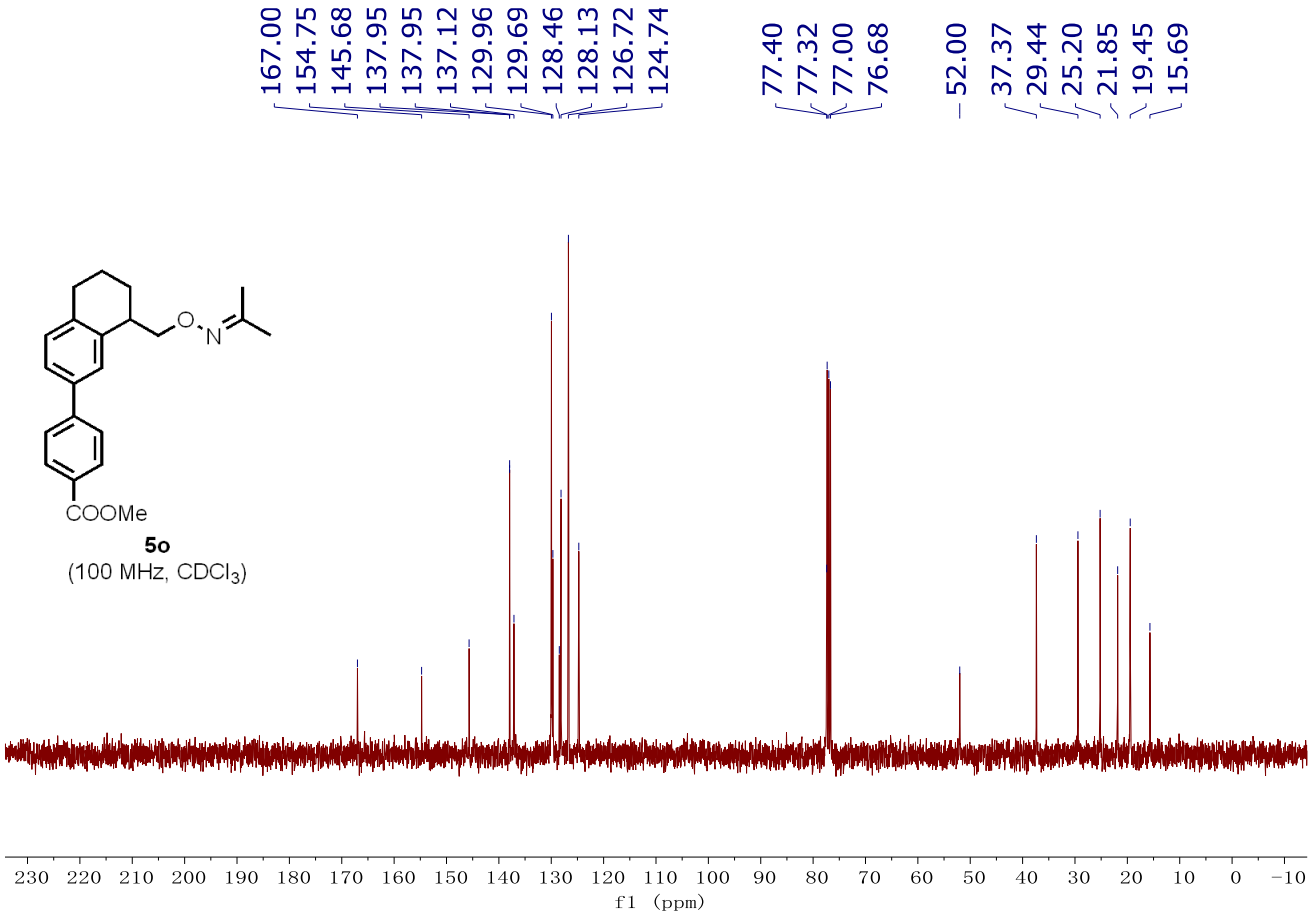

8.054
8.033
7.629
7.608
7.370
7.261
7.180
4.292
4.276
4.260
3.924
3.216
3.200
3.183
1.900
1.893
1.625
0.000
S
O
N
MeOOC
5m
(400 MHz, CDCl3)
2.04
2.10
0.95
0.99
2.10
3.12
2.10
3.00
2.97
f1 (ppm)

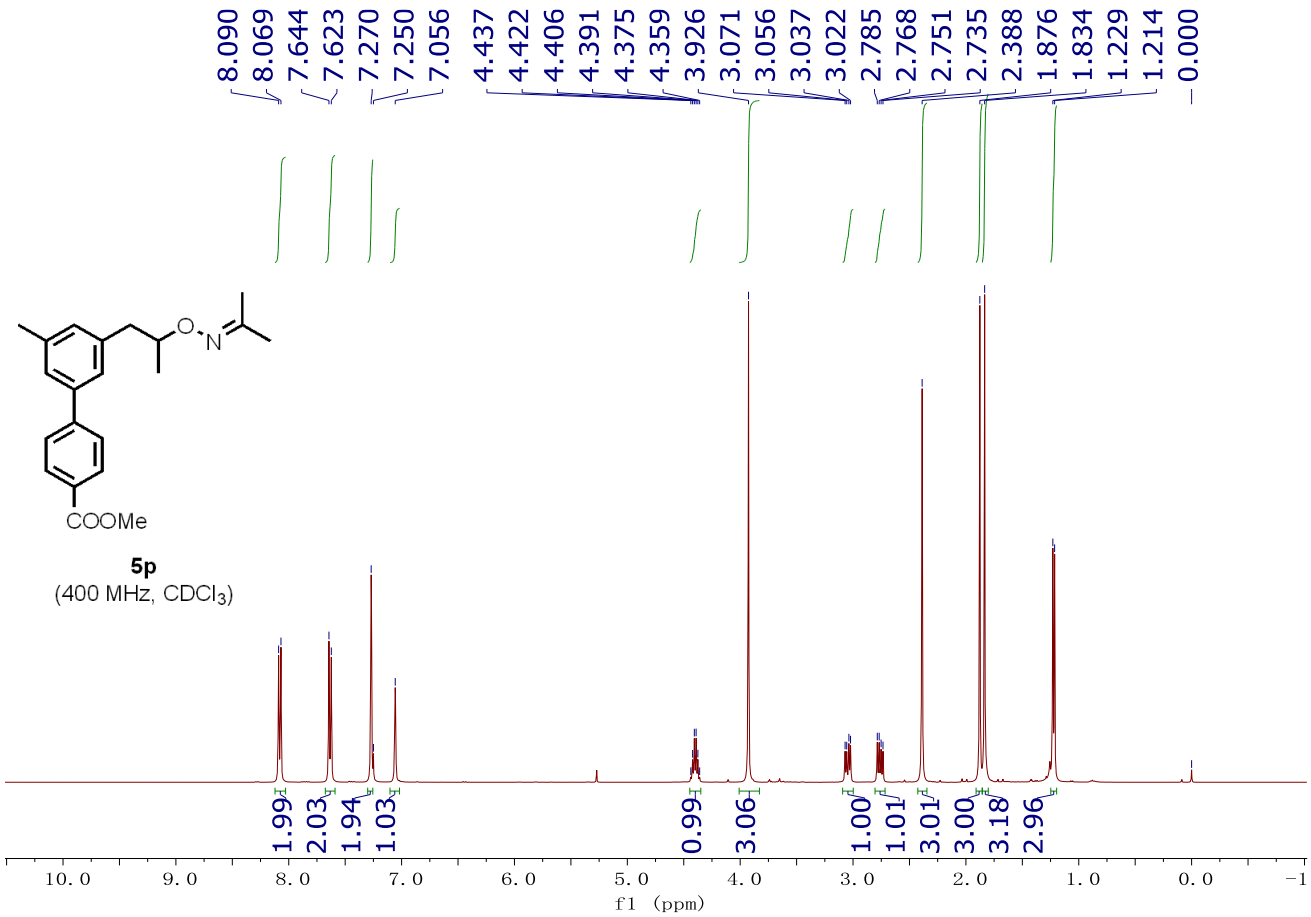

166.92
155.35
142.72
140.59
140.27
130.14
128.37
125.95
124.32
120.33
77.32
77.00
76.68
73.19
52.07
30.18
21.87
15.82
S
O
N
MeOOC
5m
(100 MHz, CDCl3)
f1 (ppm)

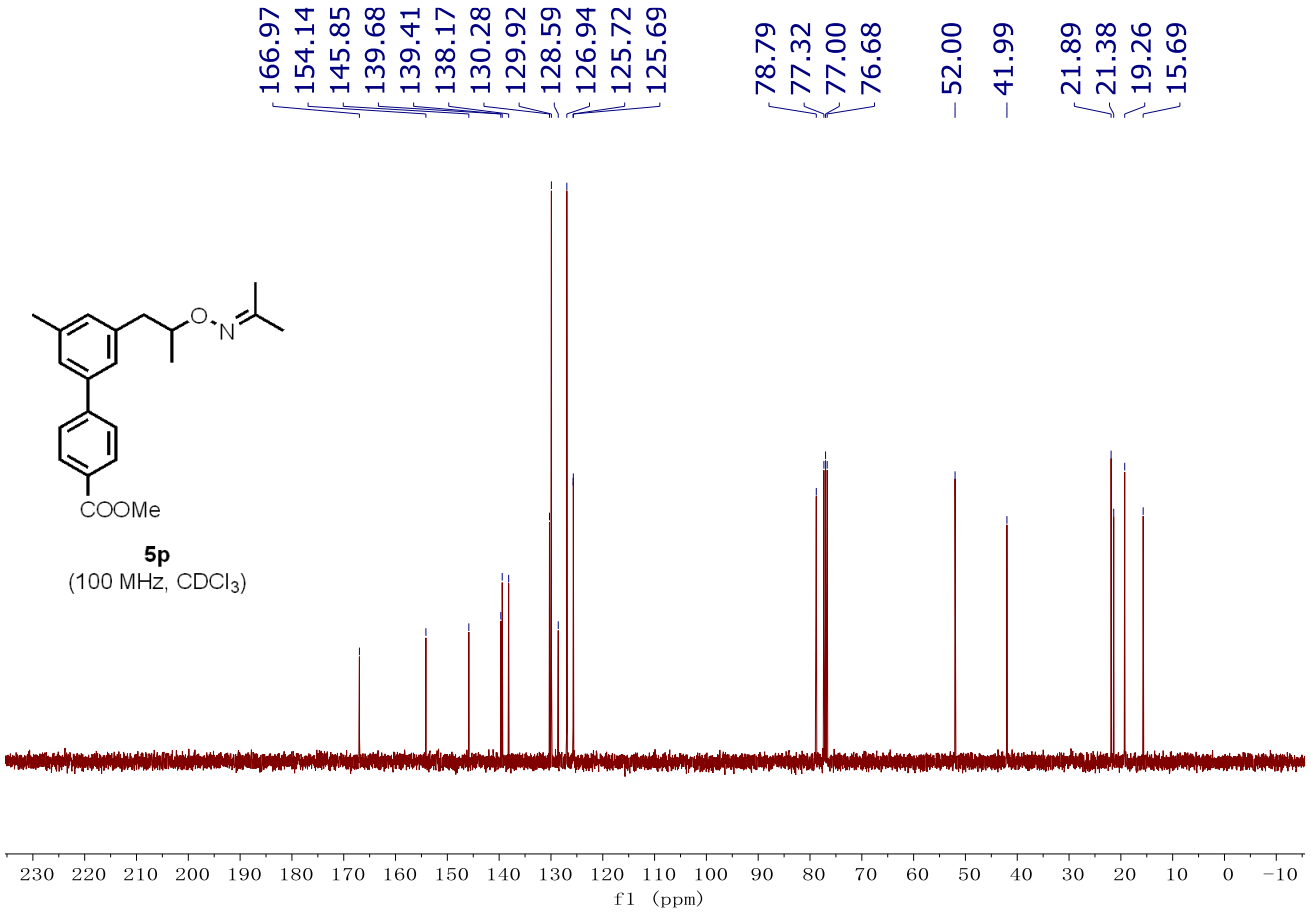

8.096
8.075
7.649
7.628
7.283
7.253
7.088
4.191
4.175
4.165
4.149
4.104
4.085
4.079
4.059
3.932
3.238
3.221
3.203
3.186
3.168
3.151
2.405
1.871
1.804
1.345
1.328
0.000
COOMe
5n
(400 MHz, CDCl3)
2.03
2.04
2.01
1.00
0.94
0.96
3.00
0.97
3.07
2.99
2.83
2.94
f1 (ppm)

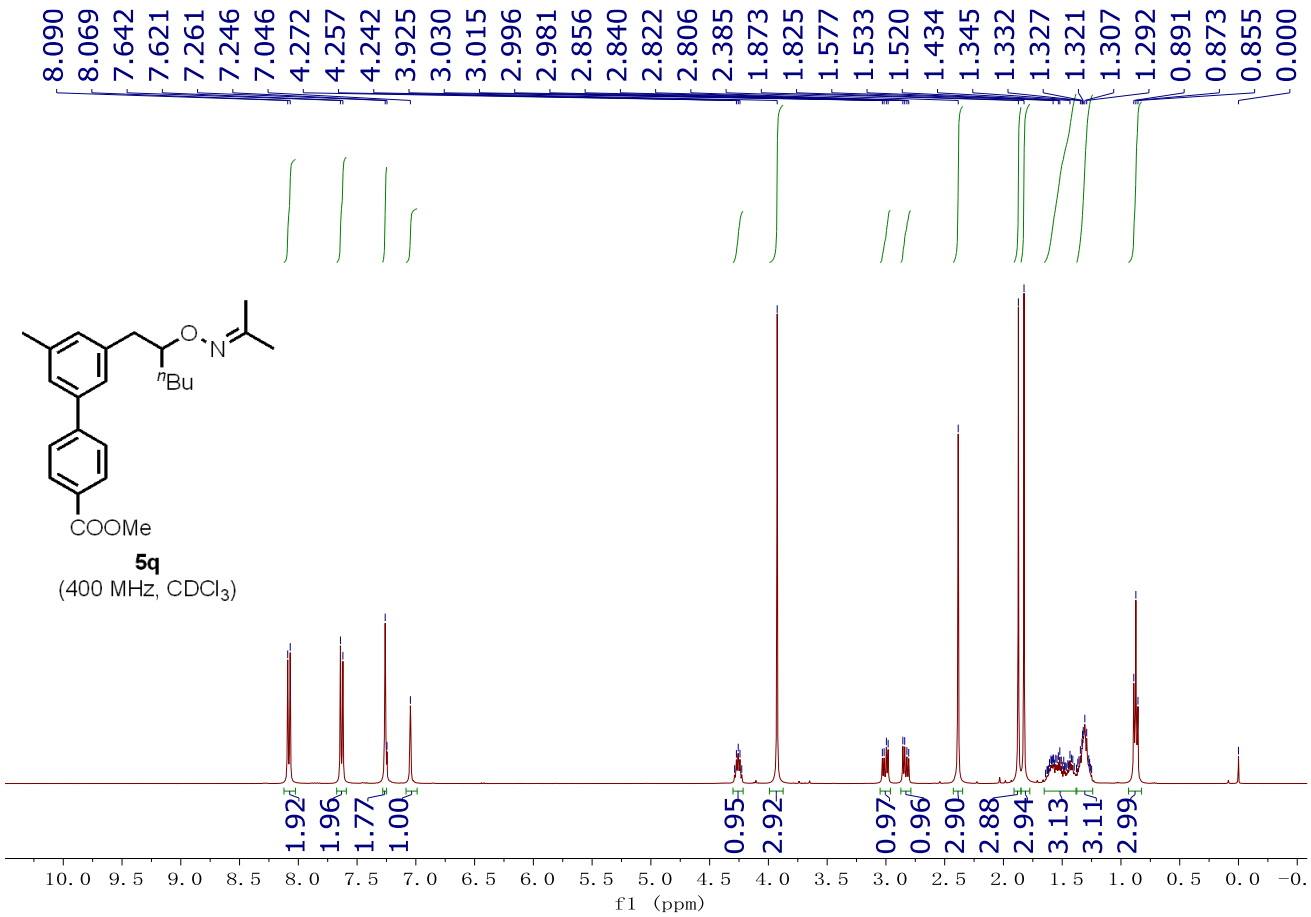

167.00
154.79
145.95
144.93
139.89
138.39
129.94
128.64
128.06
127.01
126.05
123.69
78.60
77.32
77.00
76.68
52.04
39.26
21.80
21.49
17.92
15.58
COOMe
5n
(100 MHz, CDCl3)
f1 (ppm)

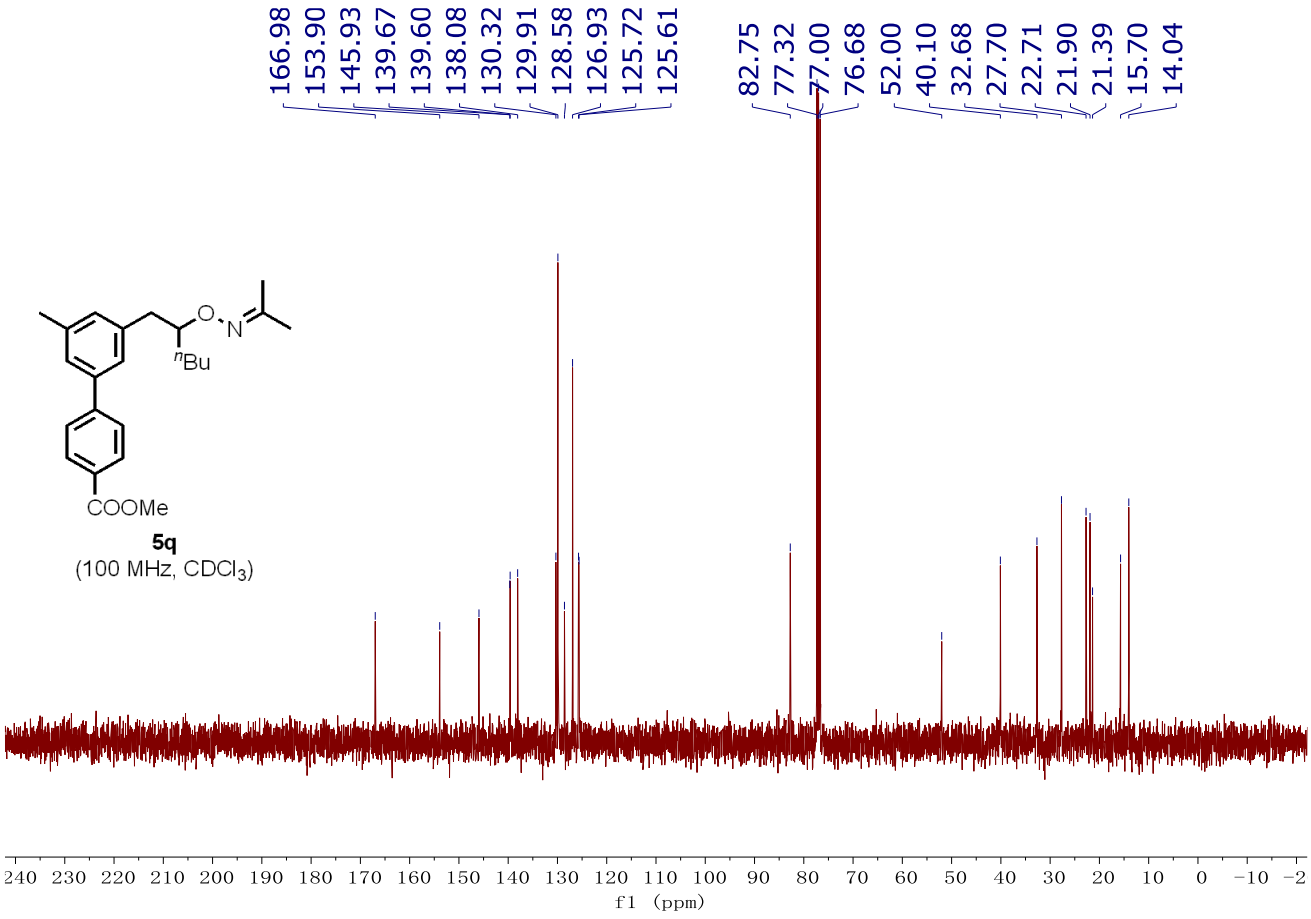

8.084
8.063
7.642
7.621
7.541
7.391
7.387
7.371
7.367
7.249
7.178
7.159
4.302
4.287
4.275
4.261
4.146
4.125
4.120
4.098
3.928
3.294
3.282
3.274
3.262
2.810
2.798
2.785
1.918
1.897
1.879
1.855
1.800
1.784
1.776
0.000
COOMe
5o
(400 MHz, CDCl3)
1.99
2.03
1.00
1.02
1.01
1.02
1.03
3.09
1.02
2.09
9.02
1.11
f1 (ppm)

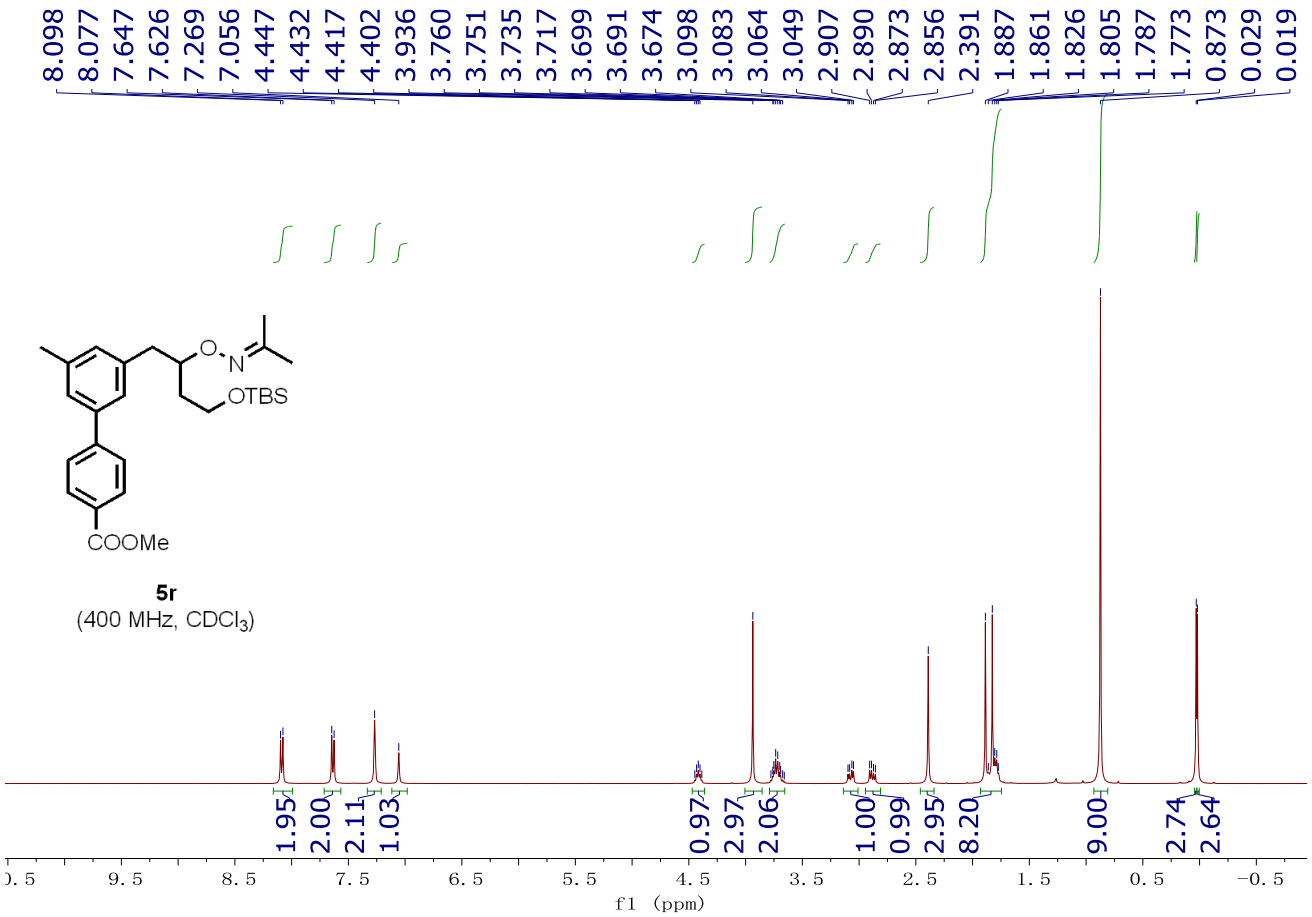

167.00
154.75
145.68
137.95
137.95
137.12
129.96
129.69
128.46
128.13
126.72
124.74
77.40
77.32
77.00
76.68
52.00
37.37
29.44
25.20
21.85
19.45
15.69
COOMe
5o
(100 MHz, CDCl3)
f1 (ppm)

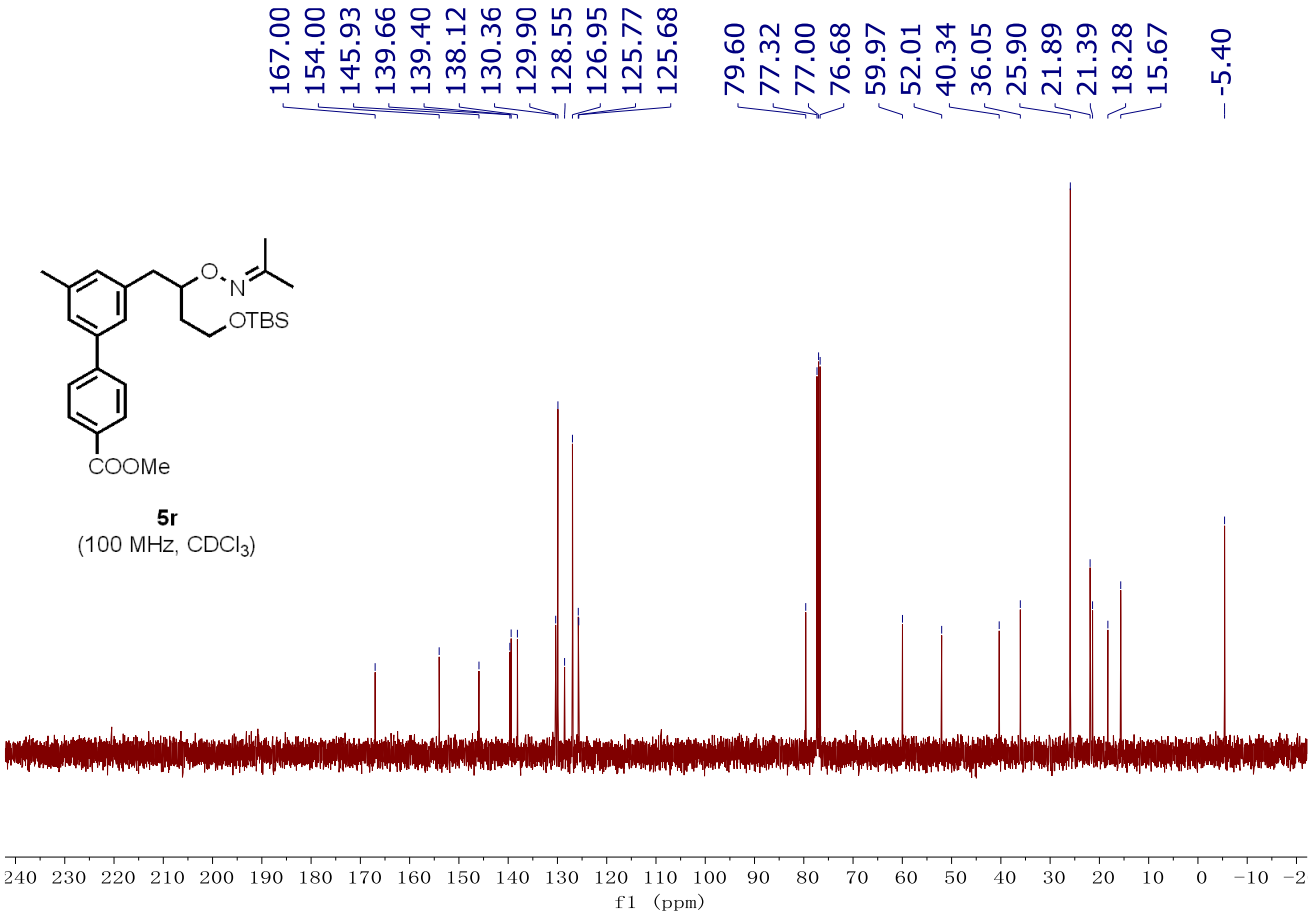

8.090
8.069
7.644
7.623
7.270
7.250
7.056
4.437
4.422
4.406
4.391
4.375
4.359
3.926
3.071
3.056
3.037
3.022
2.785
2.768
2.751
2.735
2.388
1.876
1.834
1.229
1.214
0.000
O
N
COOMe
5p
(400 MHz, CDCl3)
1.99
2.03
1.94
1.03
0.99
3.06
1.00
1.01
3.01
3.00
3.18
2.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)

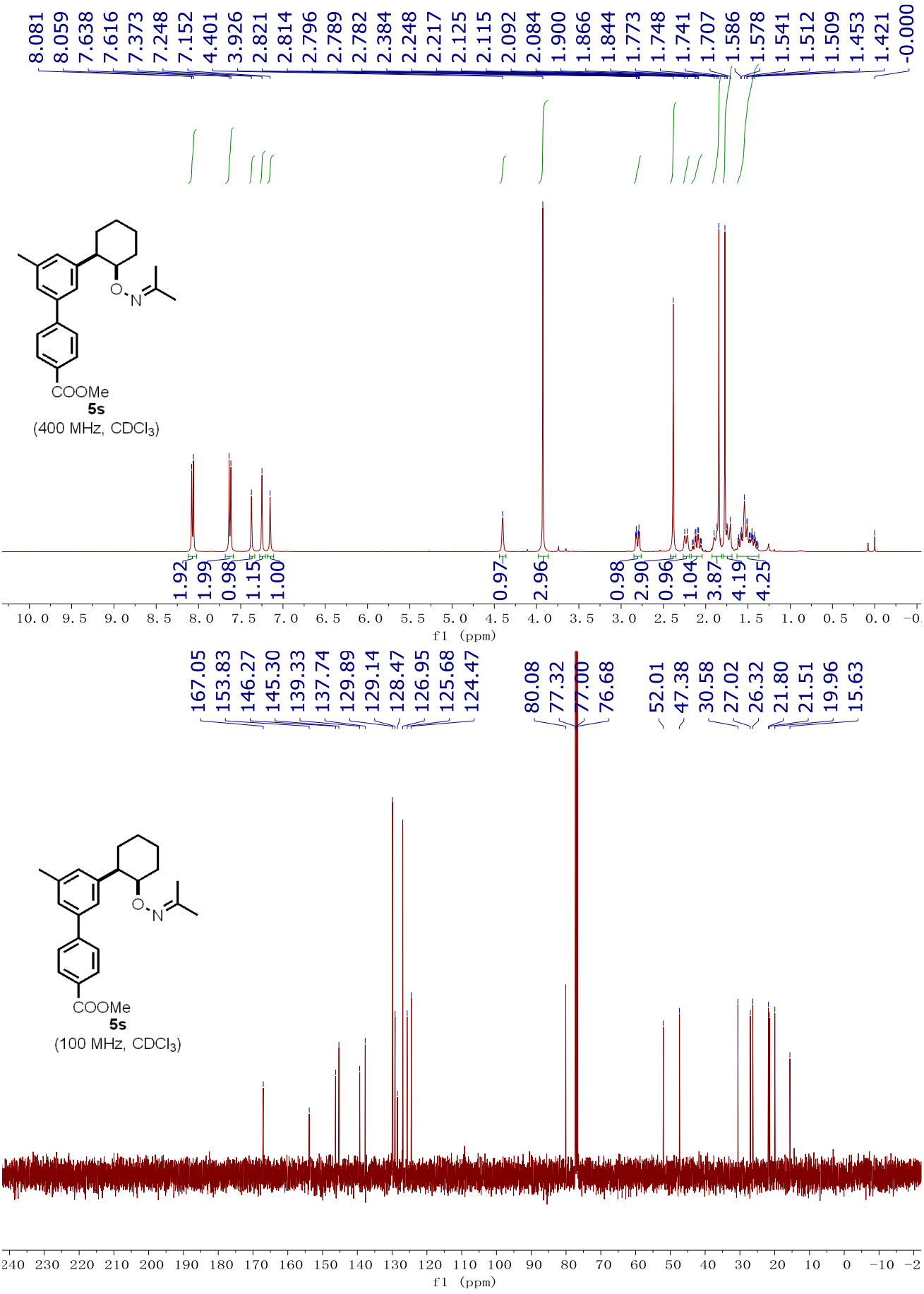

166.97
154.14
145.85
139.68
139.41
138.17
130.28
129.92
128.59
126.94
125.72
125.69
78.79
77.32
77.00
76.68
52.00
41.99
21.89
21.38
19.26
15.69
O
N
COOMe
5p
(100 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

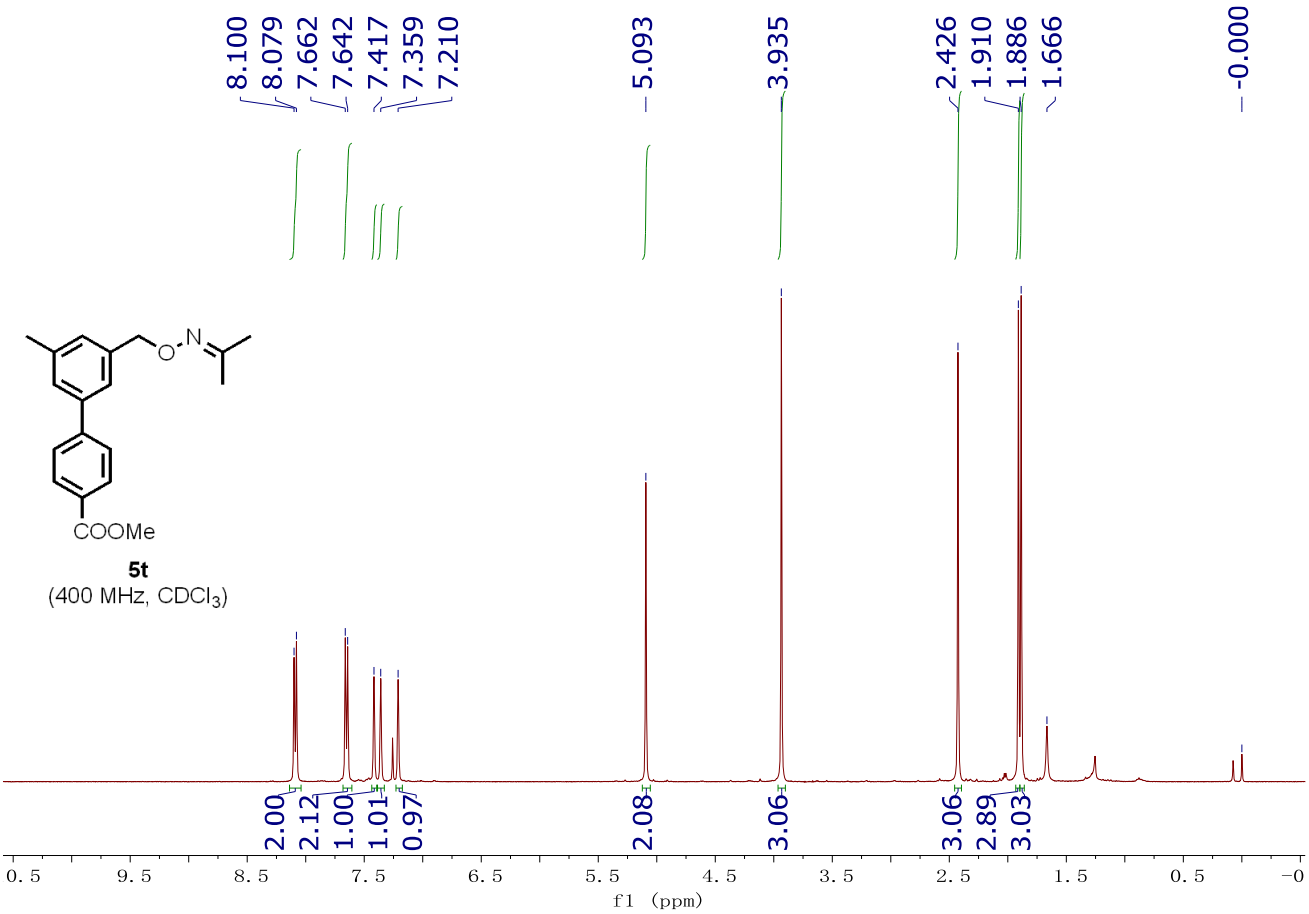

8.090
8.069
7.642
7.621
7.261
7.246
7.046
4.272
4.257
4.242
3.925
3.030
3.015
2.996
2.981
2.856
2.840
2.822
2.806
2.385
1.873
1.825
1.577
1.533
1.520
1.434
1.345
1.332
1.327
1.321
1.307
1.292
0.891
0.873
0.855
0.000
O
N
nBu
COOMe
5q
(400 MHz, CDCl3)
1.92
1.96
1.77
1.00
0.95
2.92
0.97
0.96
2.90
2.88
2.94
3.13
3.11
2.99
f1 (ppm)

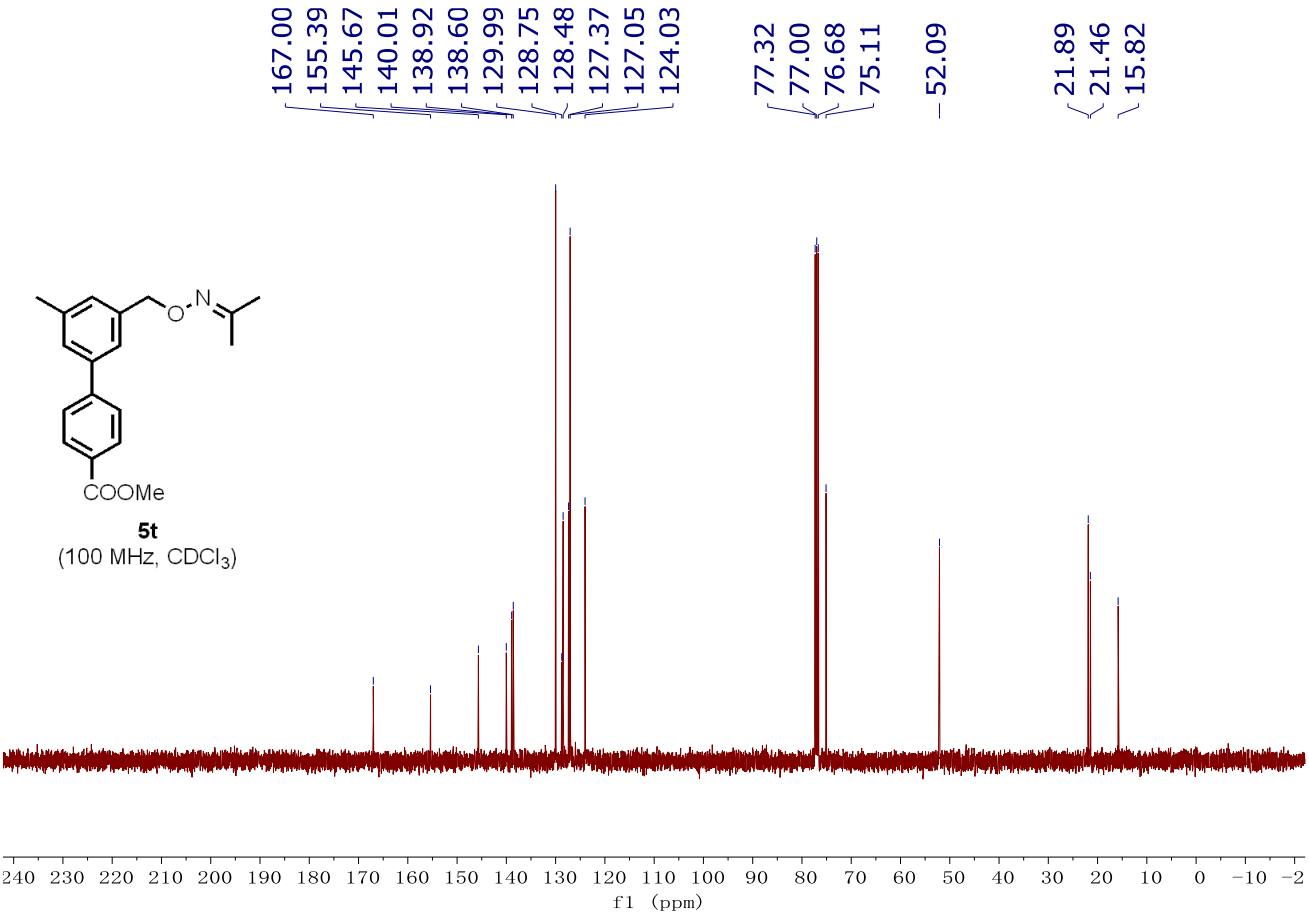

166.98
153.90
145.93
139.67
139.60
138.08
130.32
129.91
128.58
126.93
125.72
125.61
82.75
77.32
77.00
76.68
52.00
40.10
32.68
27.70
22.71
21.90
21.39
15.70
14.04
O
N
nBu
COOMe
5q
(100 MHz, CDCl3)
f1 (ppm)

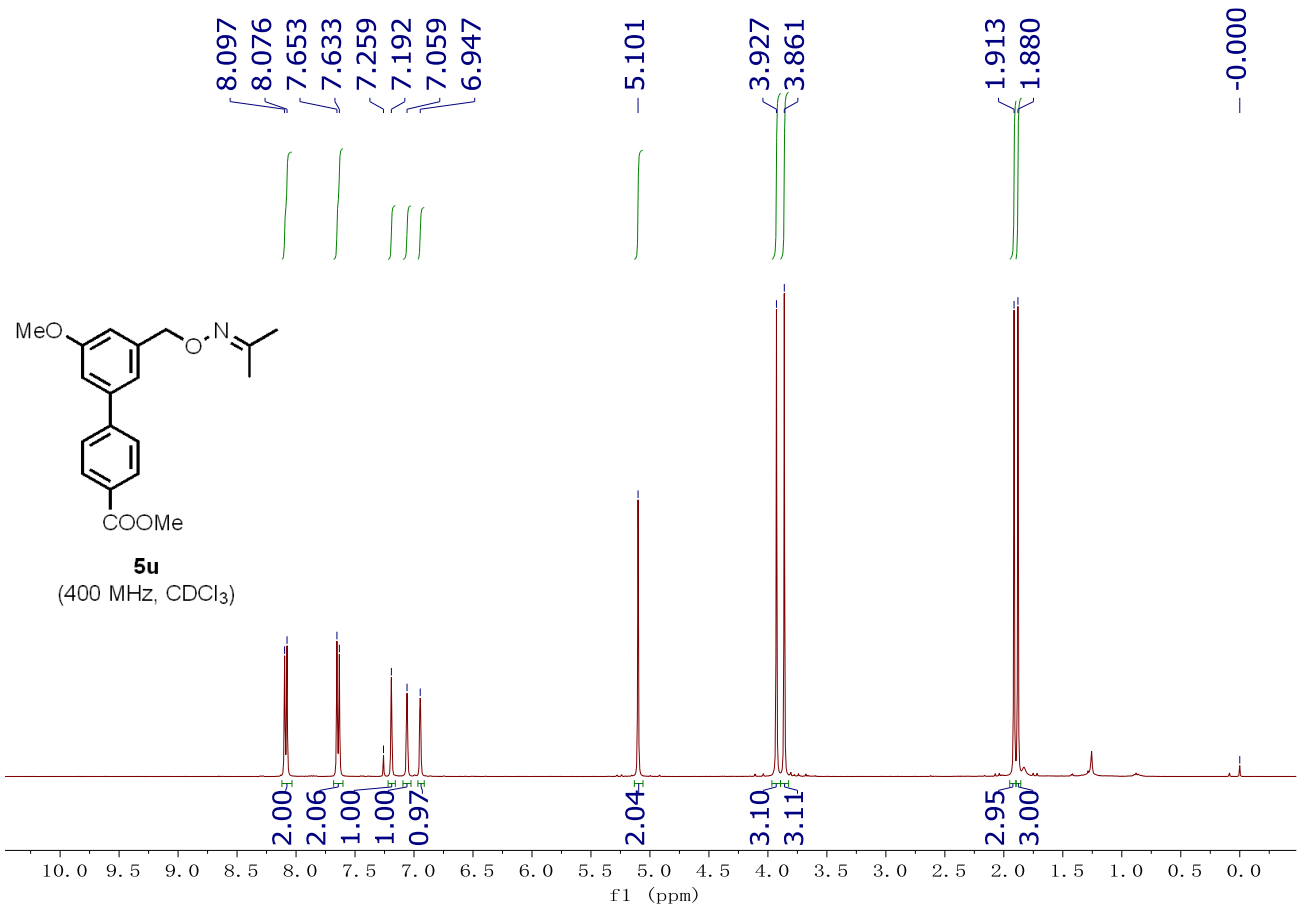

8.098
8.077
7.647
7.626
7.269
7.056
4.447
4.432
4.417
4.402
3.936
3.760
3.751
3.735
3.717
3.699
3.691
3.674
3.098
3.083
3.064
3.049
2.907
2.890
2.873
2.856
2.391
1.887
1.861
1.826
1.805
1.787
1.773
0.873
0.029
0.019
O
N
OTBS
COOMe
5r
(400 MHz, CDCl3)
1.95
2.00
2.11
1.03
0.97
2.97
2.06
1.00
0.99
2.95
8.20
9.00
2.74
2.64
f1 (ppm)

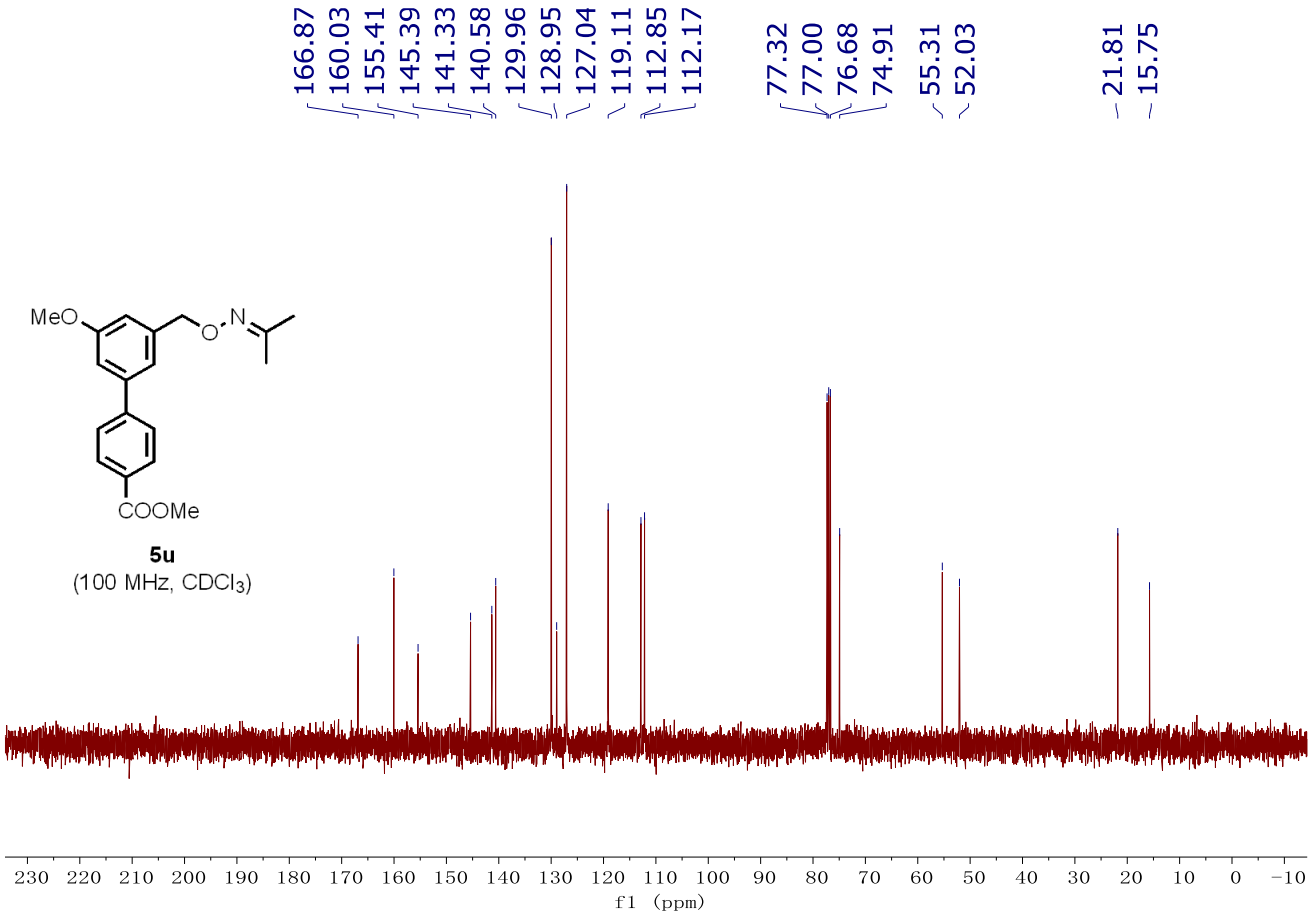

167.00
154.00
145.93
139.66
139.40
138.12
130.36
129.90
128.55
126.95
125.77
125.68
79.60
77.32
77.00
76.68
59.97
52.01
40.34
36.05
25.90
21.89
21.39
18.28
15.67
-5.40
O
N
OTBS
COOMe
5r
(100 MHz, CDCl3)
f1 (ppm)

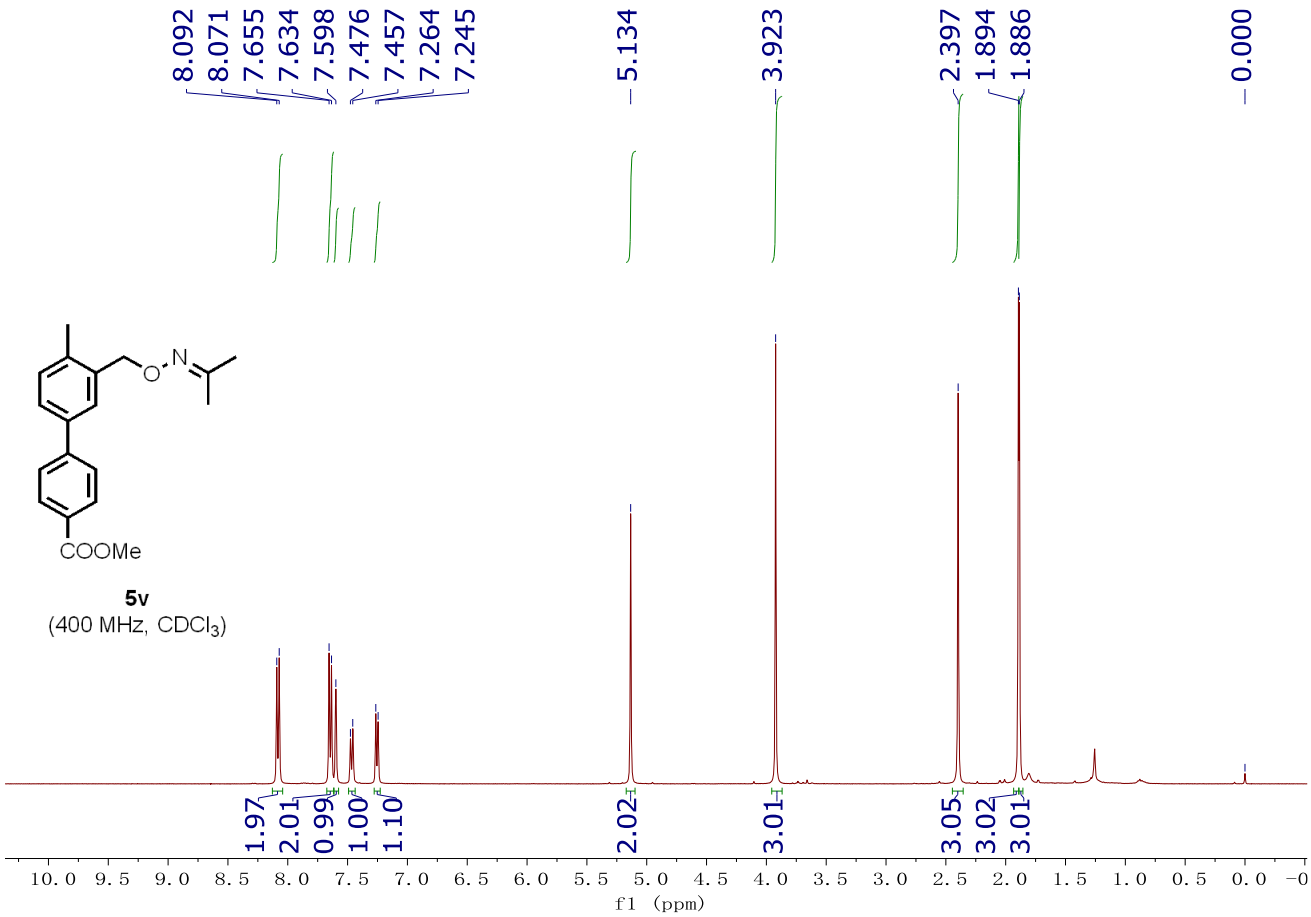

8.081
8.059
7.638
7.616
7.373
7.248
7.152
4.401
3.926
2.821
2.814
2.796
2.789
2.782
2.384
2.248
2.217
2.125
2.115
2.092
2.084
1.900
1.866
1.844
1.773
1.748
1.741
1.707
1.586
1.578
1.541
1.512
1.509
1.453
1.421
-0.000
COOMe
5s
(400 MHz, CDCl3)
1.92
1.99
0.98
1.15
1.00
0.97
2.96
0.98
2.90
0.96
1.04
3.87
4.19
4.25
f1 (ppm)
167.05
153.83
146.27
145.30
139.33
137.74
129.89
129.14
128.47
126.95
125.68
124.47
80.08
77.32
77.00
76.68
52.01
47.38
30.58
27.02
26.32
21.80
21.51
19.96
15.63
COOMe
5s
(100 MHz, CDCl3)
f1 (ppm)

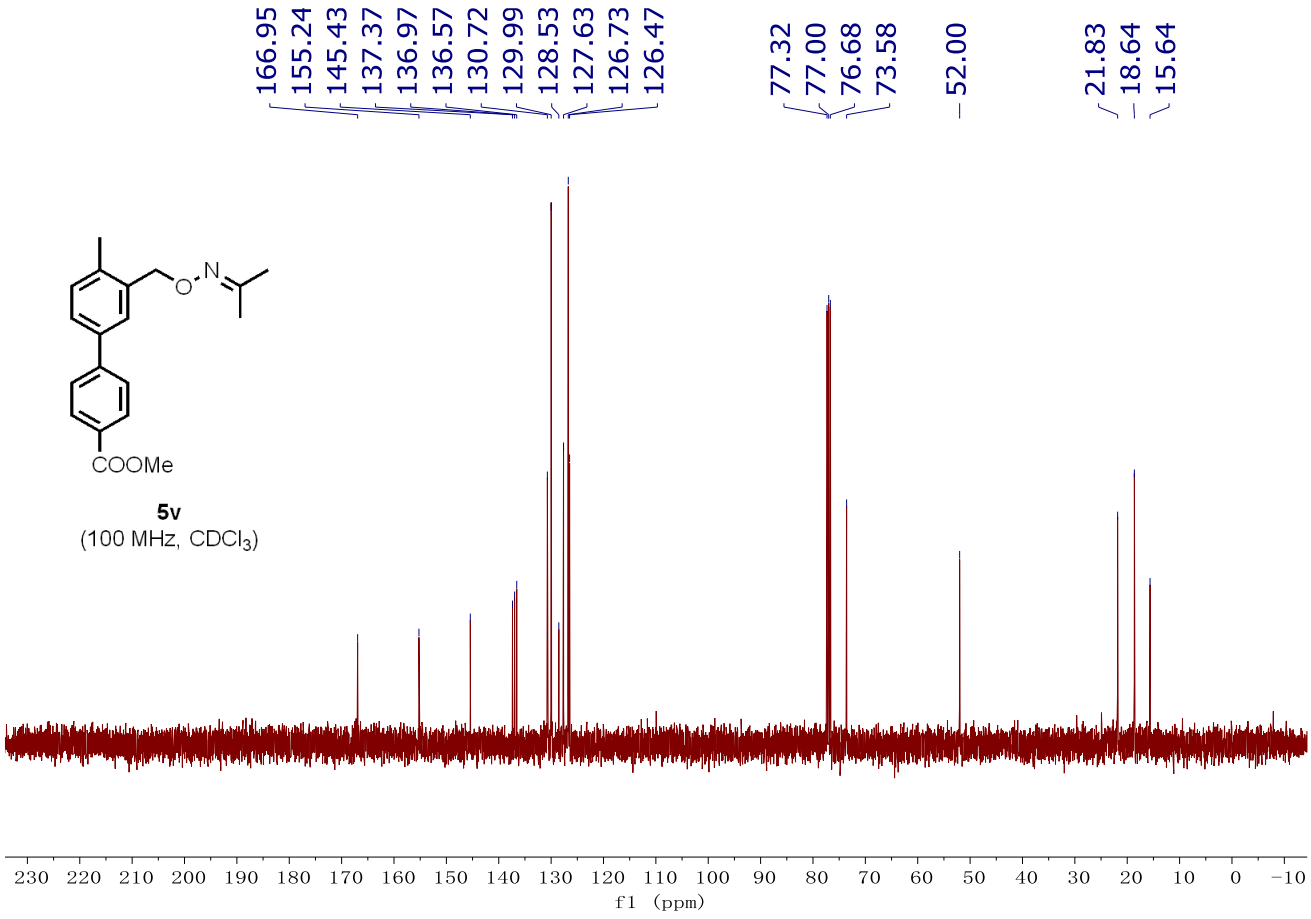

8.100
8.079
7.662
7.642
7.417
7.359
7.210
5.093
3.935
2.426
1.910
1.886
1.666
-0.000
COOMe
5t
(400 MHz, CDCl3)
2.00
2.12
1.00
1.01
0.97
2.08
3.06
3.06
2.89
3.03
f1 (ppm)

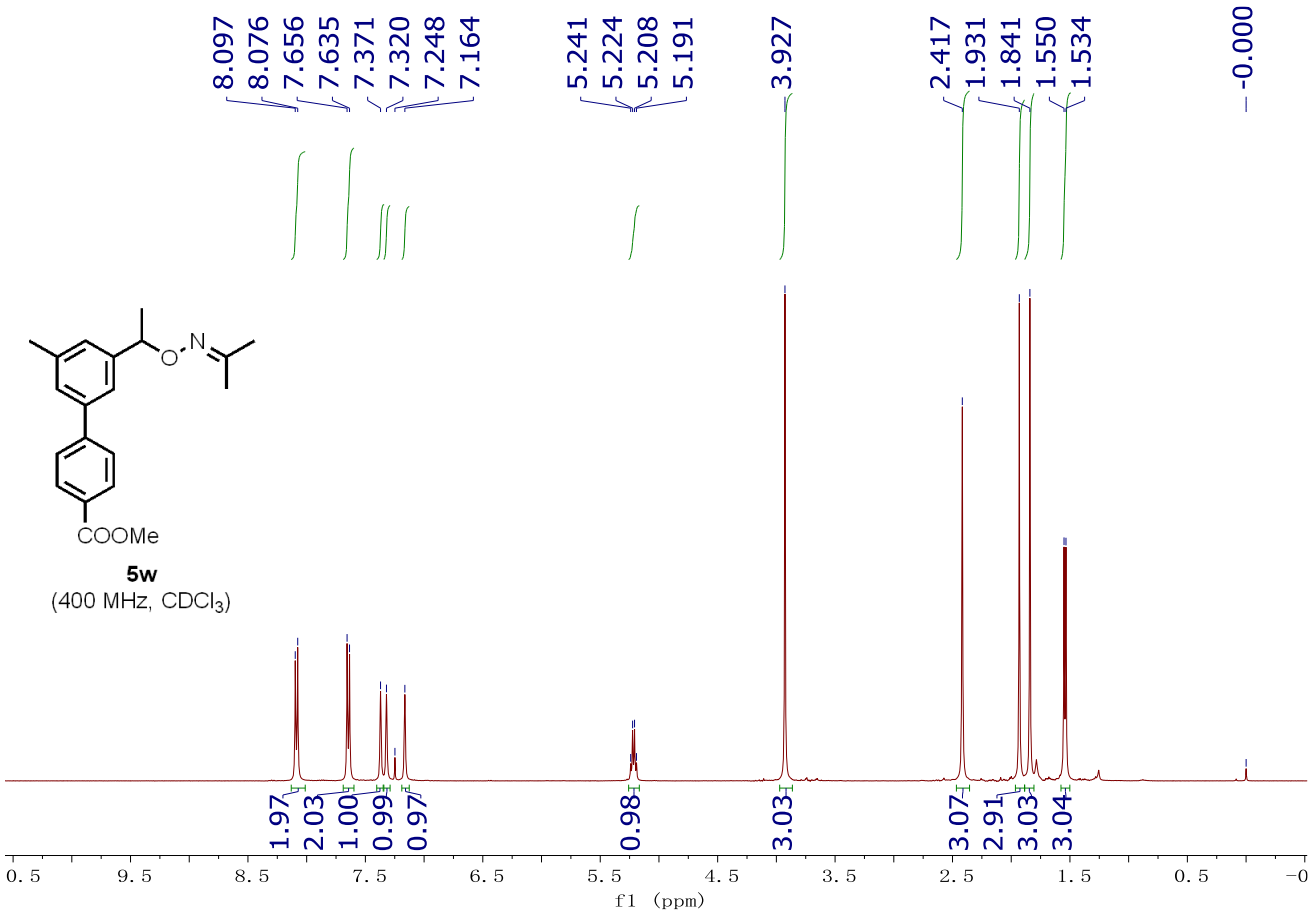

167.00
155.39
145.67
140.01
138.92
138.60
129.99
128.75
128.48
127.37
127.05
124.03
77.32
77.00
76.68
75.11
52.09
21.89
21.46
15.82
COOMe
5t
(100 MHz, CDCl3)
f1 (ppm)

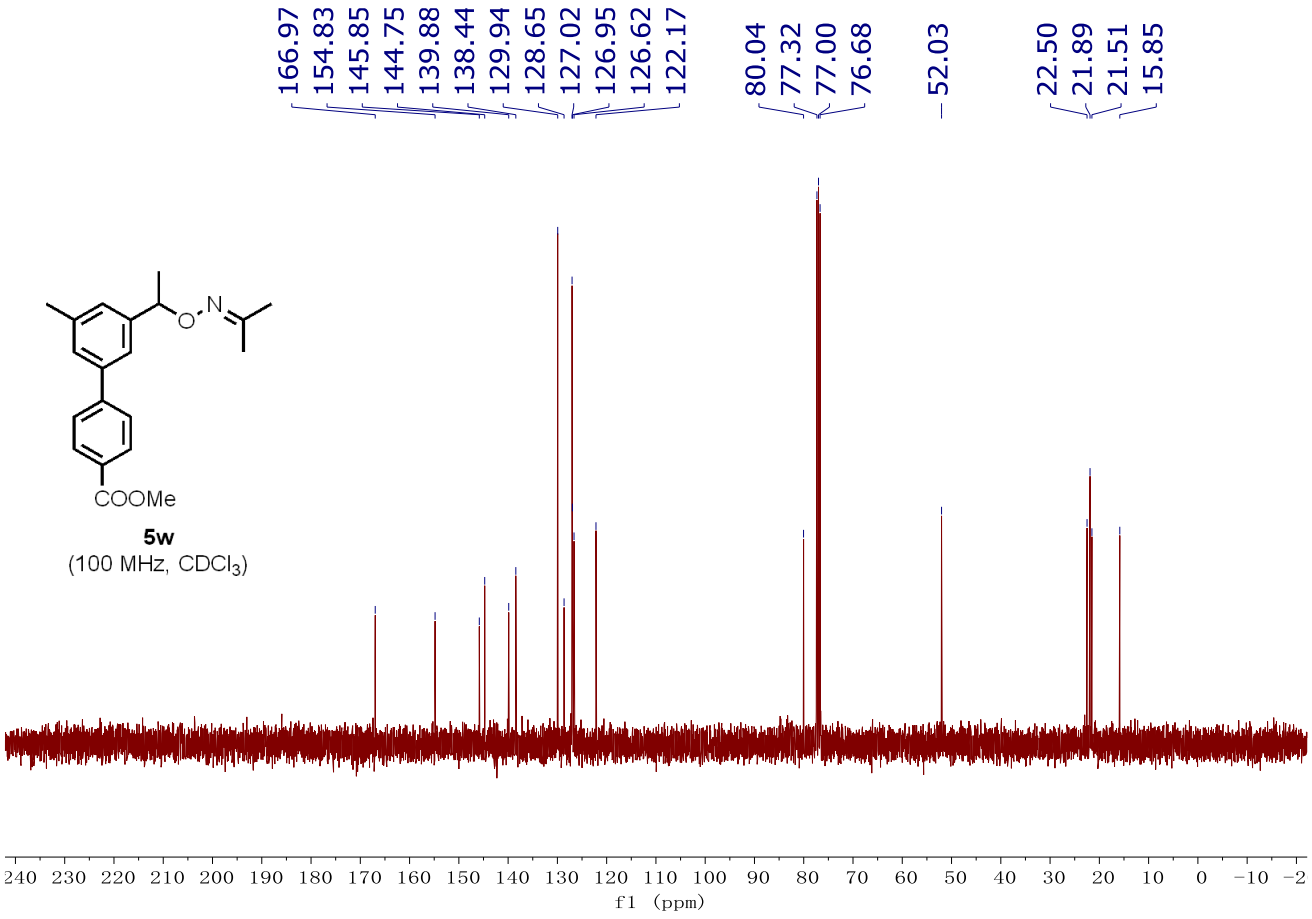

8.097
8.076
7.653
7.633
7.259
7.192
7.059
6.947
5.101
3.927
3.861
1.913
1.880
-0.000
MeO
O
N
COOMe
5u
(400 MHz, CDCl3)
2.00
2.06
1.00
1.00
0.97
2.04
3.10
3.11
2.95
3.00
f1 (ppm)

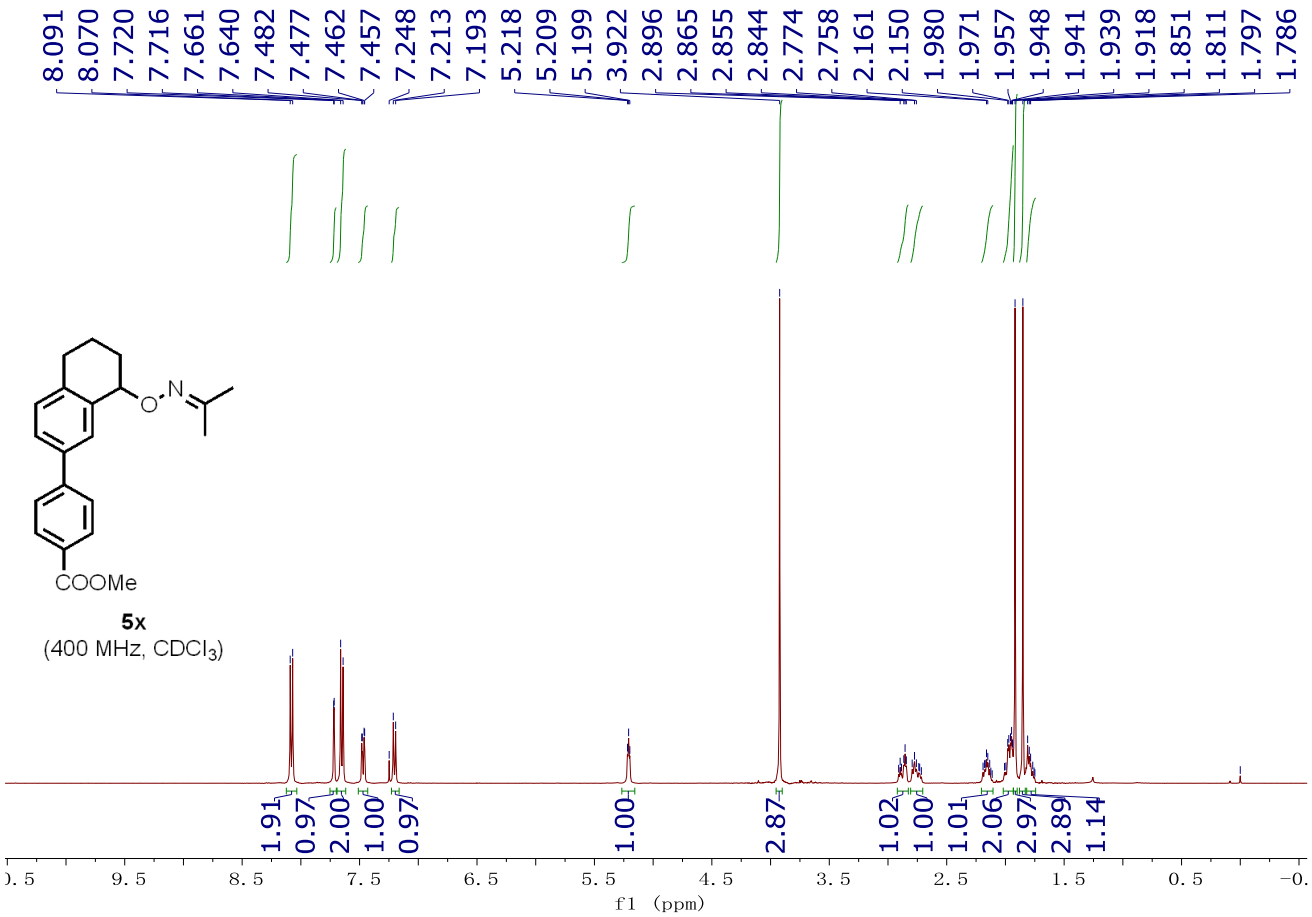

166.87
160.03
155.41
145.39
141.33
140.58
129.96
128.95
127.04
119.11
112.85
112.17
77.32
77.00
76.68
74.91
55.31
52.03
21.81
15.75
MeO
O
N
COOMe
5u
(100 MHz, CDCl3)
f1 (ppm)

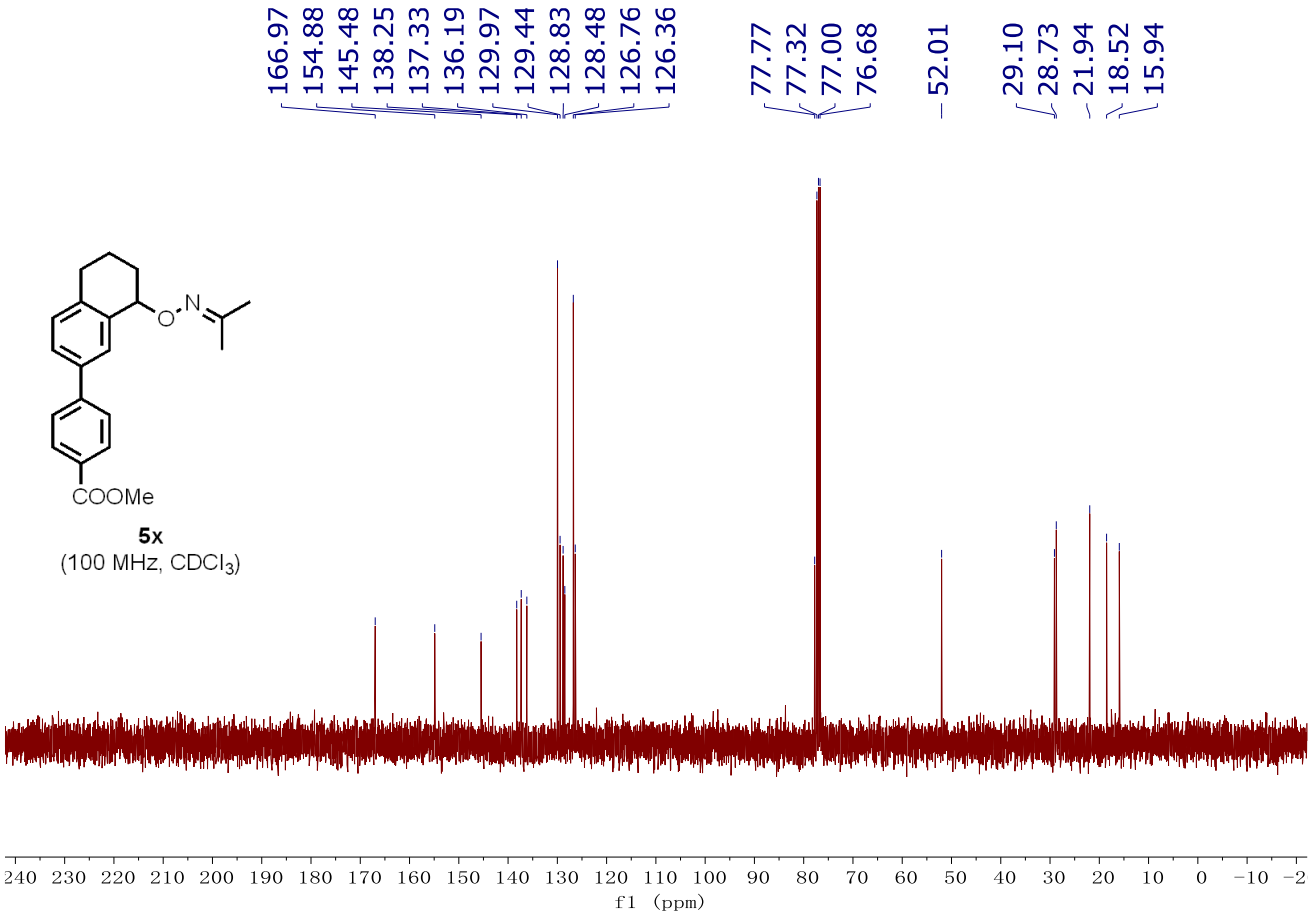

8.092
8.071
7.655
7.634
7.598
7.476
7.457
7.264
7.245
5.134
3.923
2.397
1.894
1.886
0.000
COOMe
5v
(400 MHz, CDCl3)
1.97
2.01
0.99
1.00
1.10
2.02
3.01
3.05
3.02
3.01
f1 (ppm)

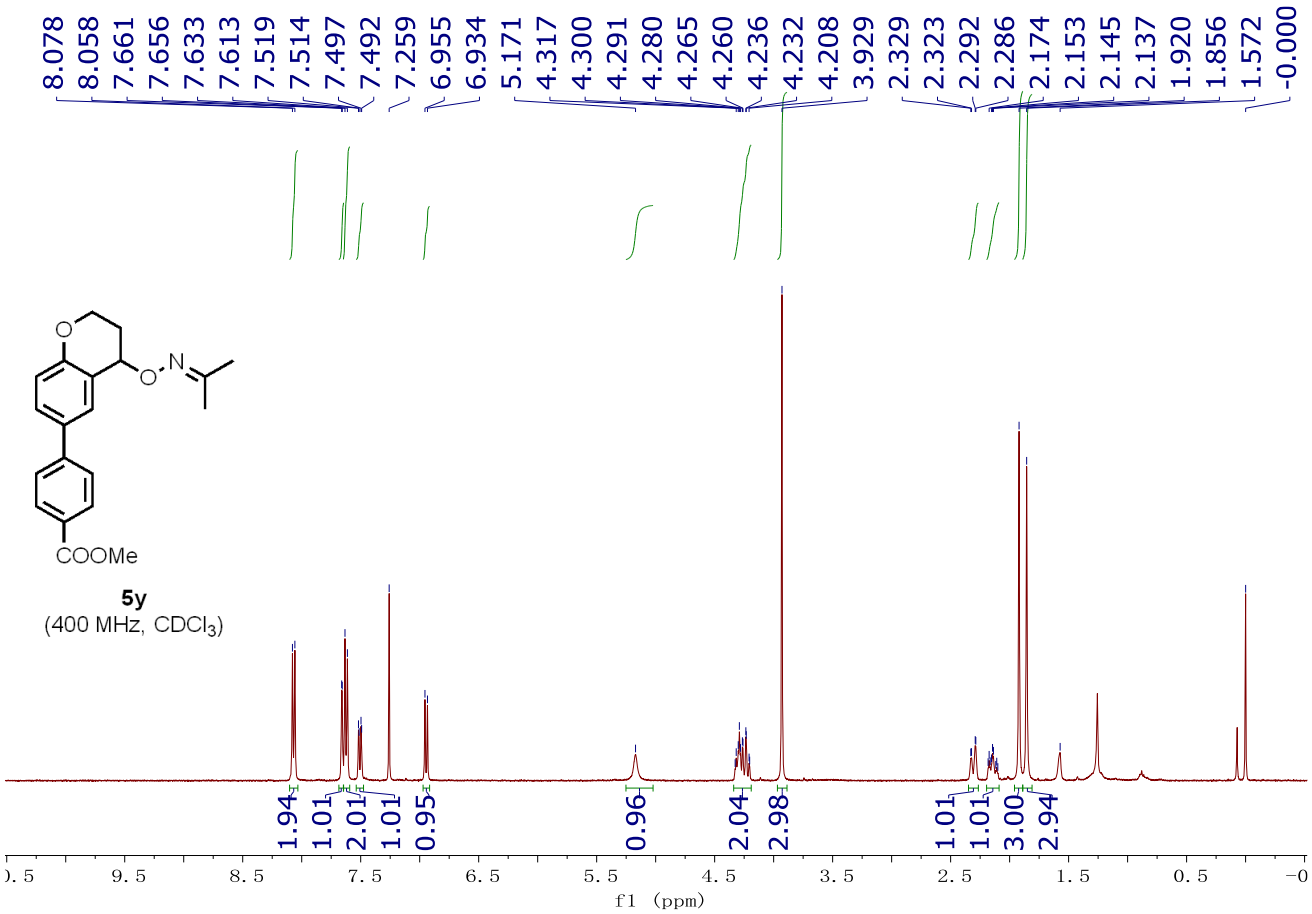

166.95
155.24
145.43
137.37
136.97
136.57
130.72
129.99
128.53
127.63
126.73
126.47
77.32
77.00
76.68
73.58
52.00
21.83
18.64
15.64
COOMe
5v
(100 MHz, CDCl3)
f1 (ppm)

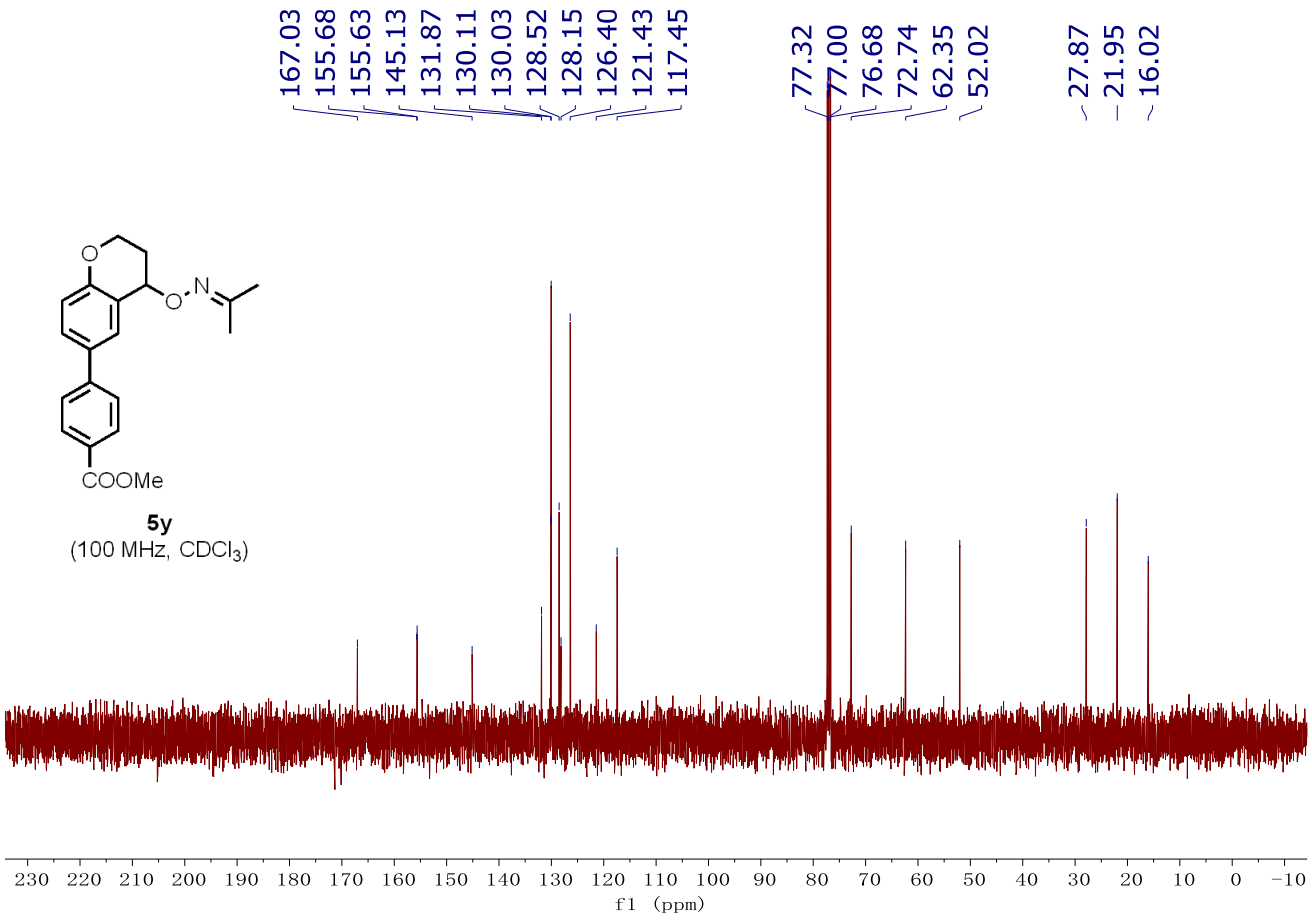

8.097
8.076
7.656
7.635
7.371
7.320
7.248
7.164
5.241
5.224
5.208
5.191
3.927
2.417
1.931
1.841
1.550
1.534
-0.000
COOMe
5w
(400 MHz, CDCl3)
1.97
2.03
1.00
0.99
0.97
0.98
3.03
3.07
2.91
3.03
3.04
f1 (ppm)

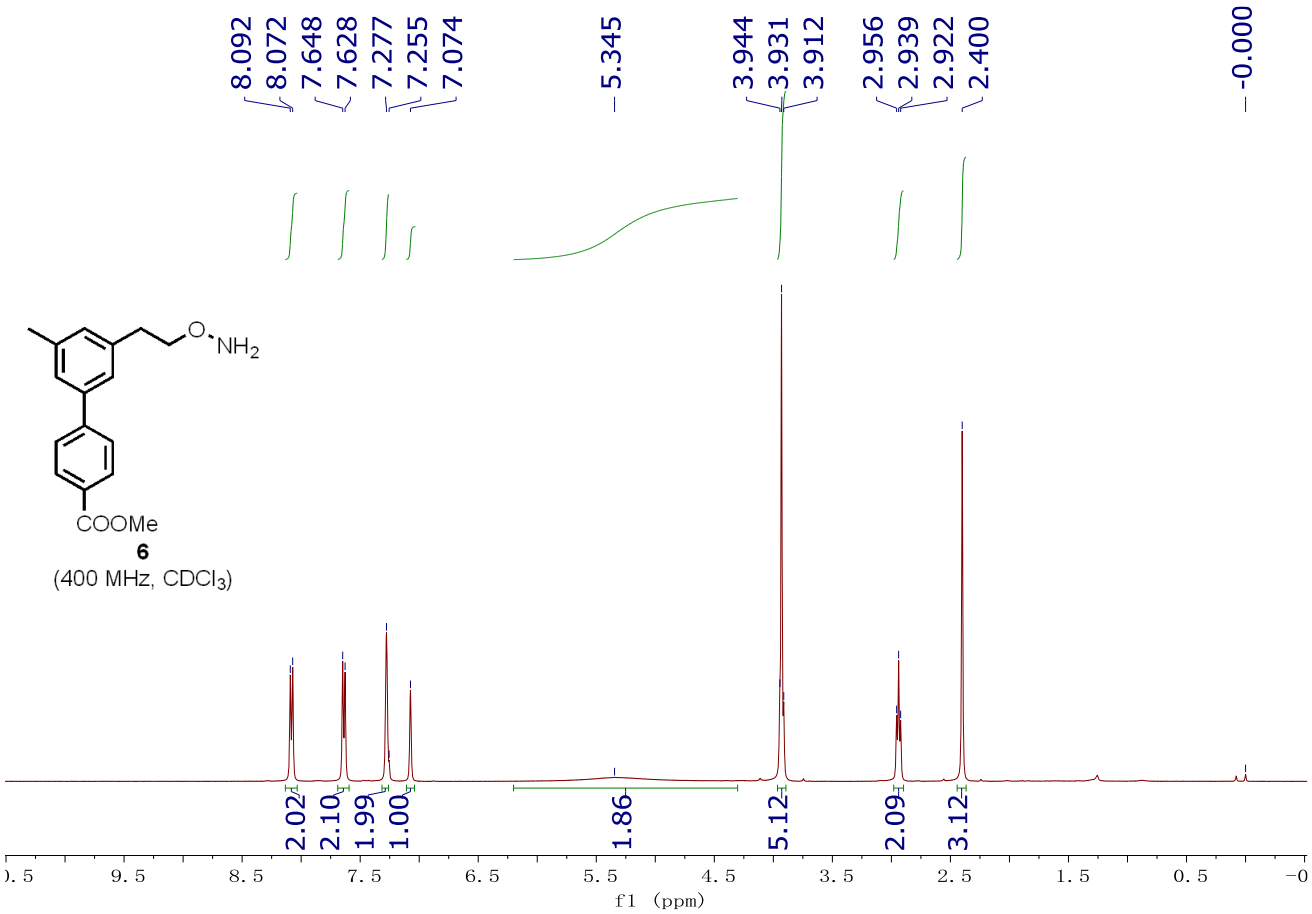

166.97
154.83
145.85
144.75
139.88
138.44
129.94
128.65
127.02
126.95
126.62
122.17
80.04
77.32
77.00
76.68
52.03
22.50
21.89
21.51
15.85
COOMe
5w
(100 MHz, CDCl3)
f1 (ppm)

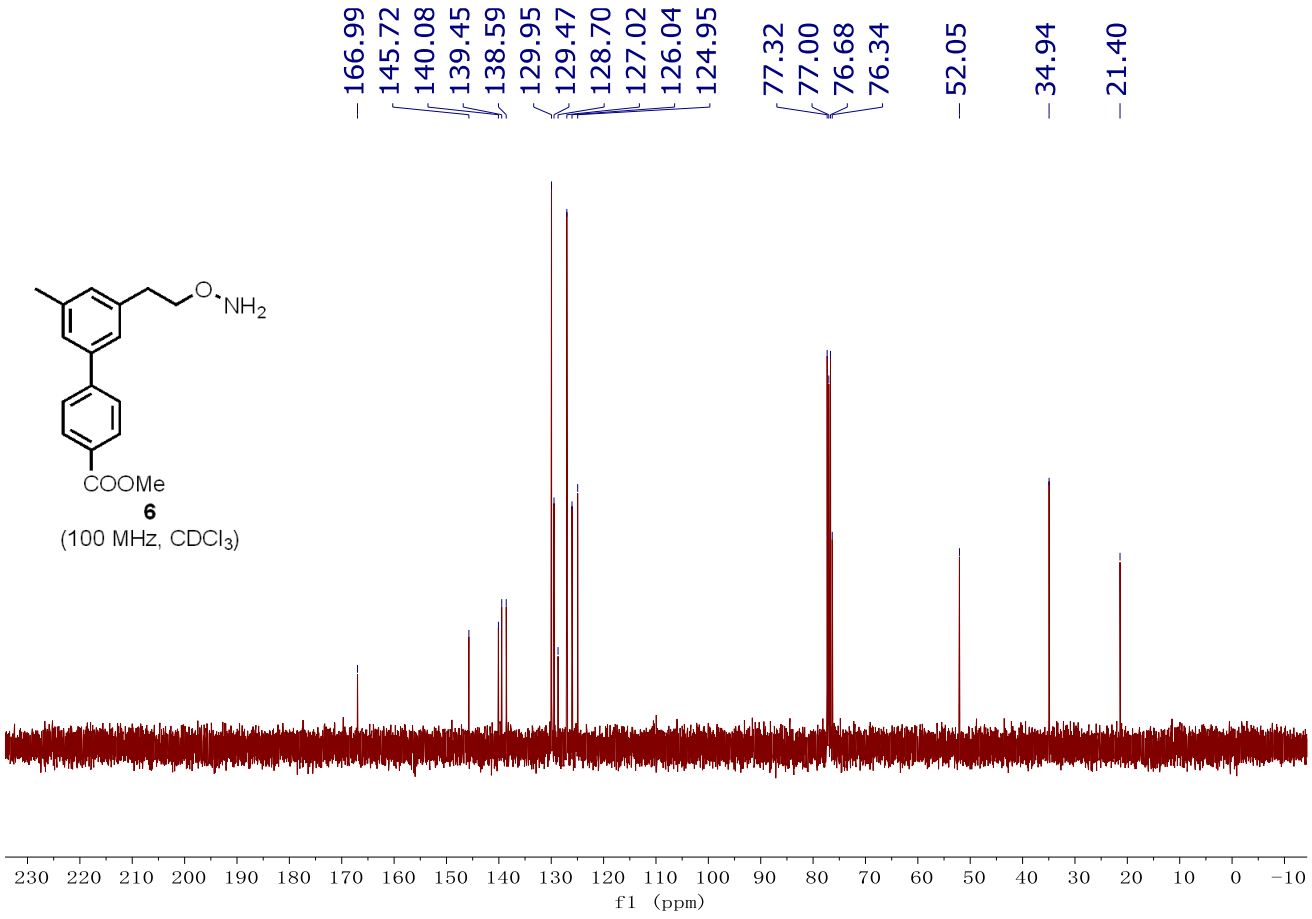

8.091
8.070
7.720
7.716
7.661
7.640
7.482
7.477
7.462
7.457
7.248
7.213
7.193
5.218
5.209
5.199
3.922
2.896
2.865
2.855
2.844
2.774
2.758
2.161
2.150
1.980
1.971
1.957
1.948
1.941
1.939
1.918
1.851
1.811
1.797
1.786
O
N
COOMe
5x
(400 MHz, CDCl3)
1.91
0.97
2.00
1.00
0.97
1.00
2.87
1.02
1.00
1.01
2.06
2.97
2.89
1.14
f1 (ppm)

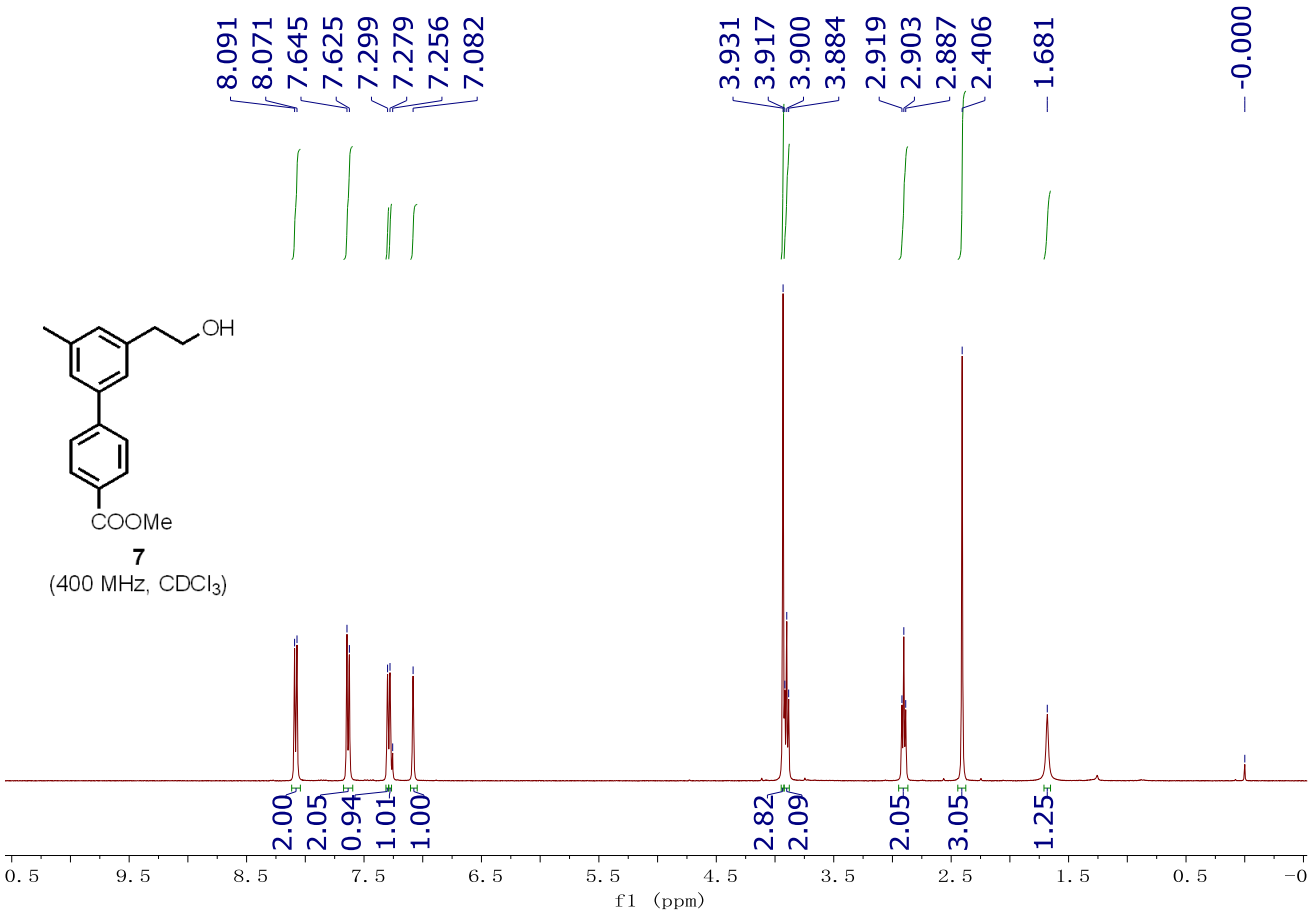

166.97
154.88
145.48
138.25
137.33
136.19
129.97
129.44
128.83
128.48
126.76
126.36
77.77
77.32
77.00
76.68
52.01
29.10
28.73
21.94
18.52
15.94
O
N
COOMe
5x
(100 MHz, CDCl3)
f1 (ppm)

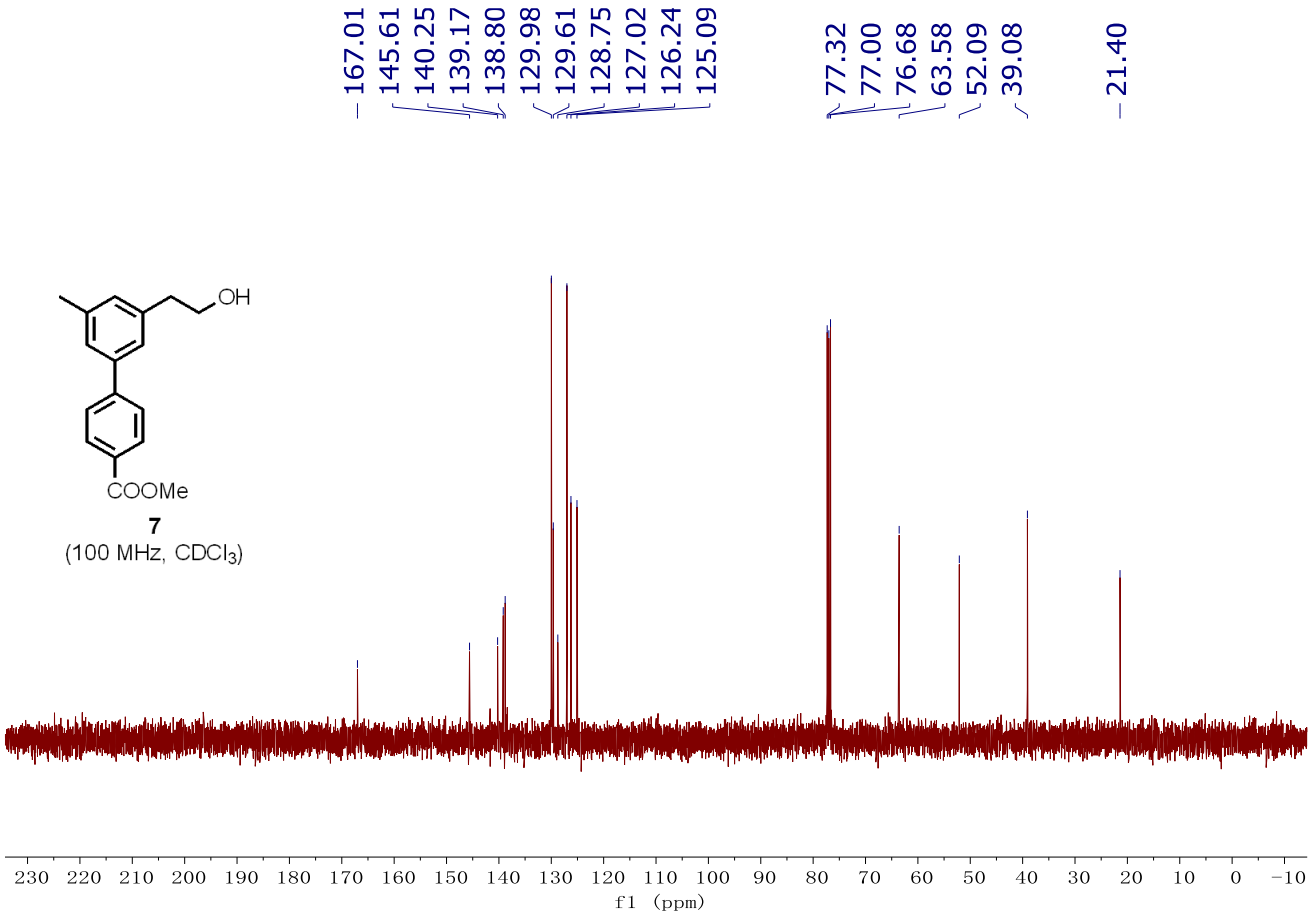

8.078
8.058
7.661
7.656
7.633
7.613
7.519
7.514
7.497
7.492
7.259
6.955
6.934
5.171
4.317
4.300
4.291
4.280
4.265
4.260
4.236
4.232
4.208
3.929
2.329
2.323
2.292
2.286
2.174
2.153
2.145
2.137
1.920
1.856
1.572
-0.000
COOMe
5y
(400 MHz, CDCl3)
1.94
1.01
2.01
1.01
0.95
0.96
2.04
2.98
1.01
1.01
3.00
2.94
f1 (ppm)

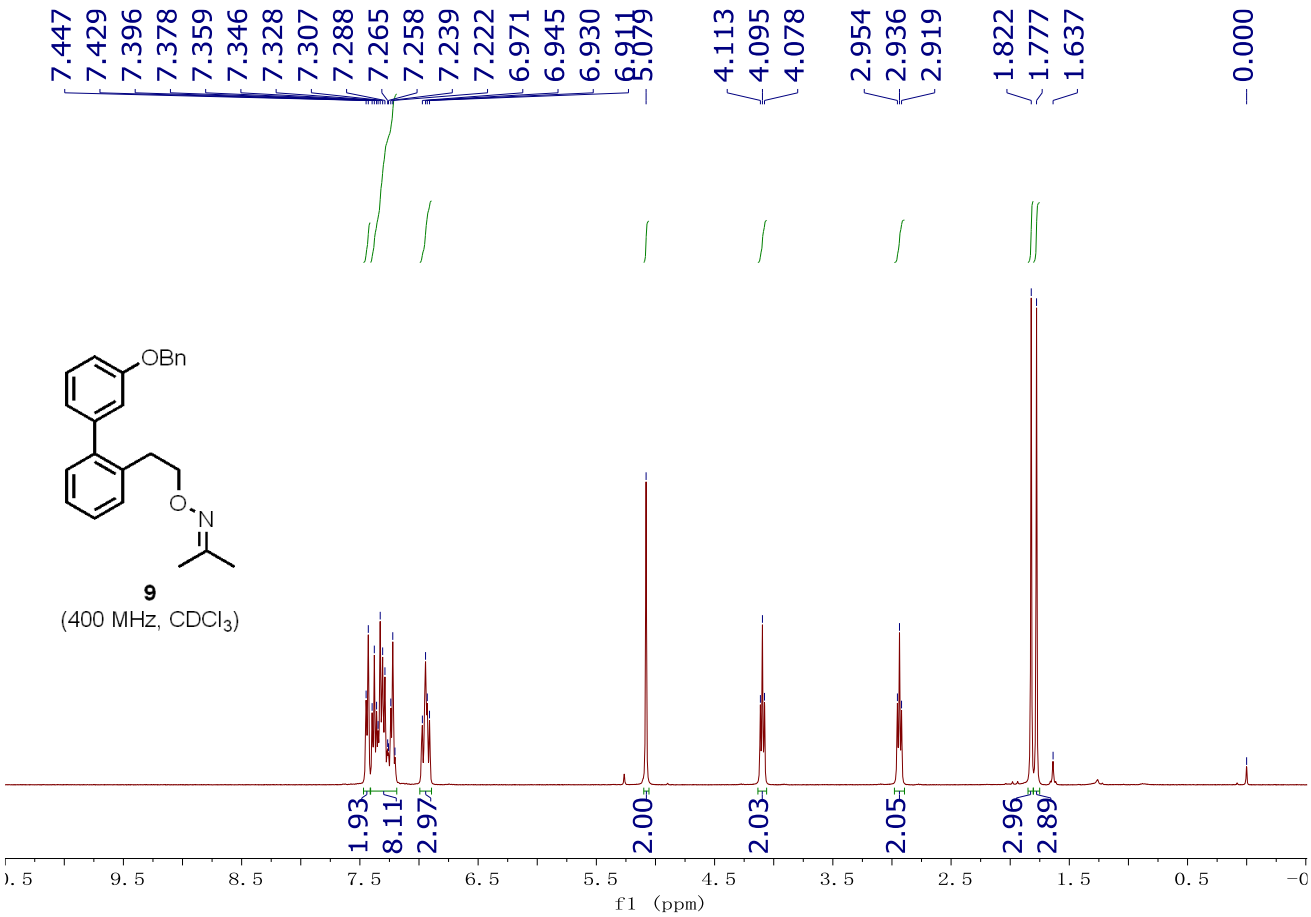

167.03
155.68
155.63
145.13
131.87
130.11
130.03
128.52
128.15
126.40
121.43
117.45
77.32
77.00
76.68
72.74
62.35
52.02
27.87
21.95
16.02
COOMe
5y
(100 MHz, CDCl3)
f1 (ppm)

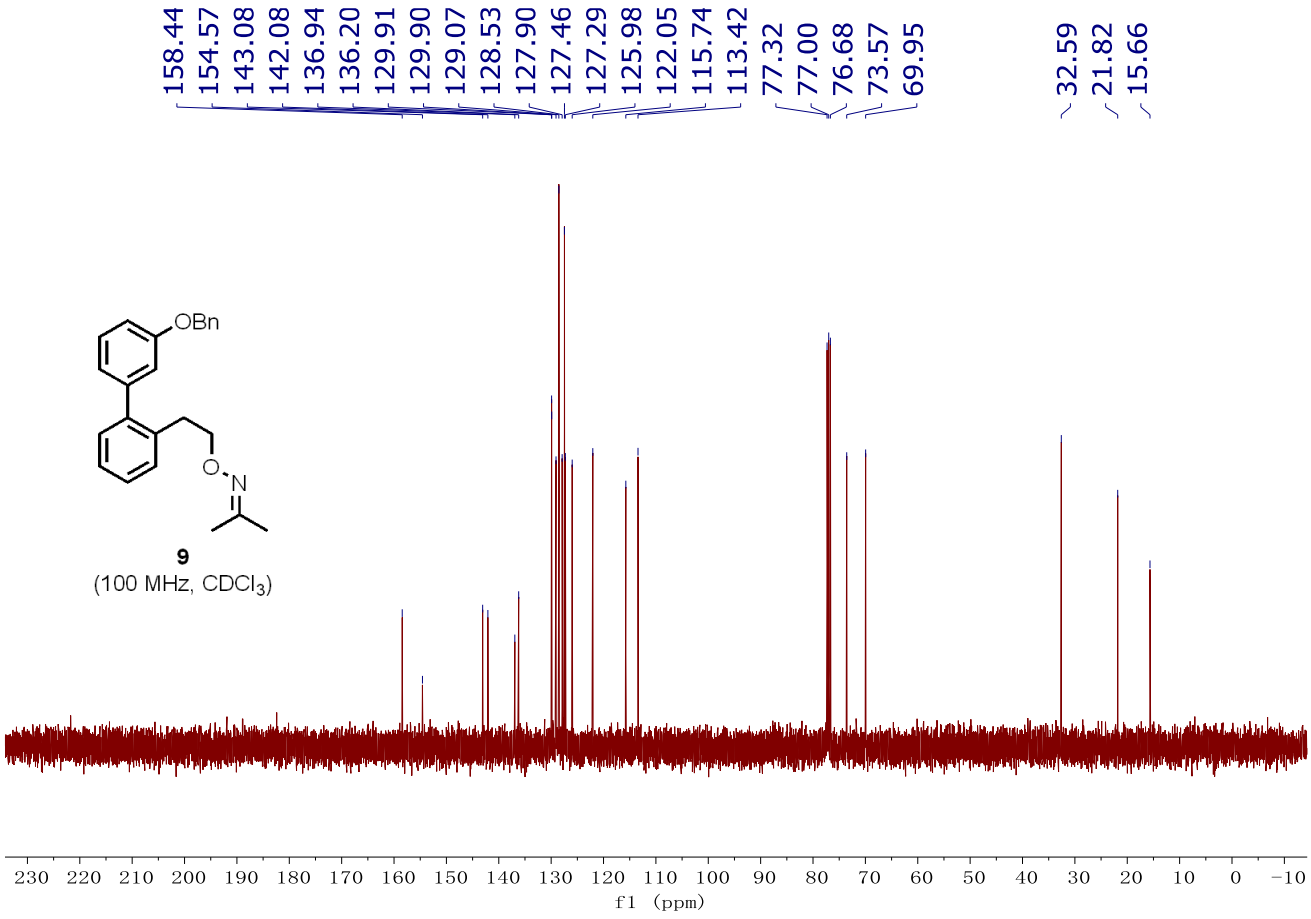

8.092
8.072
7.648
7.628
7.277
7.255
7.074
5.345
3.944
3.931
3.912
2.956
2.939
2.922
2.400
-0.000
NH2
COOMe
6
(400 MHz, CDCl3)
2.02
2.10
1.99
1.00
1.86
5.12
2.09
3.12
f1 (ppm)

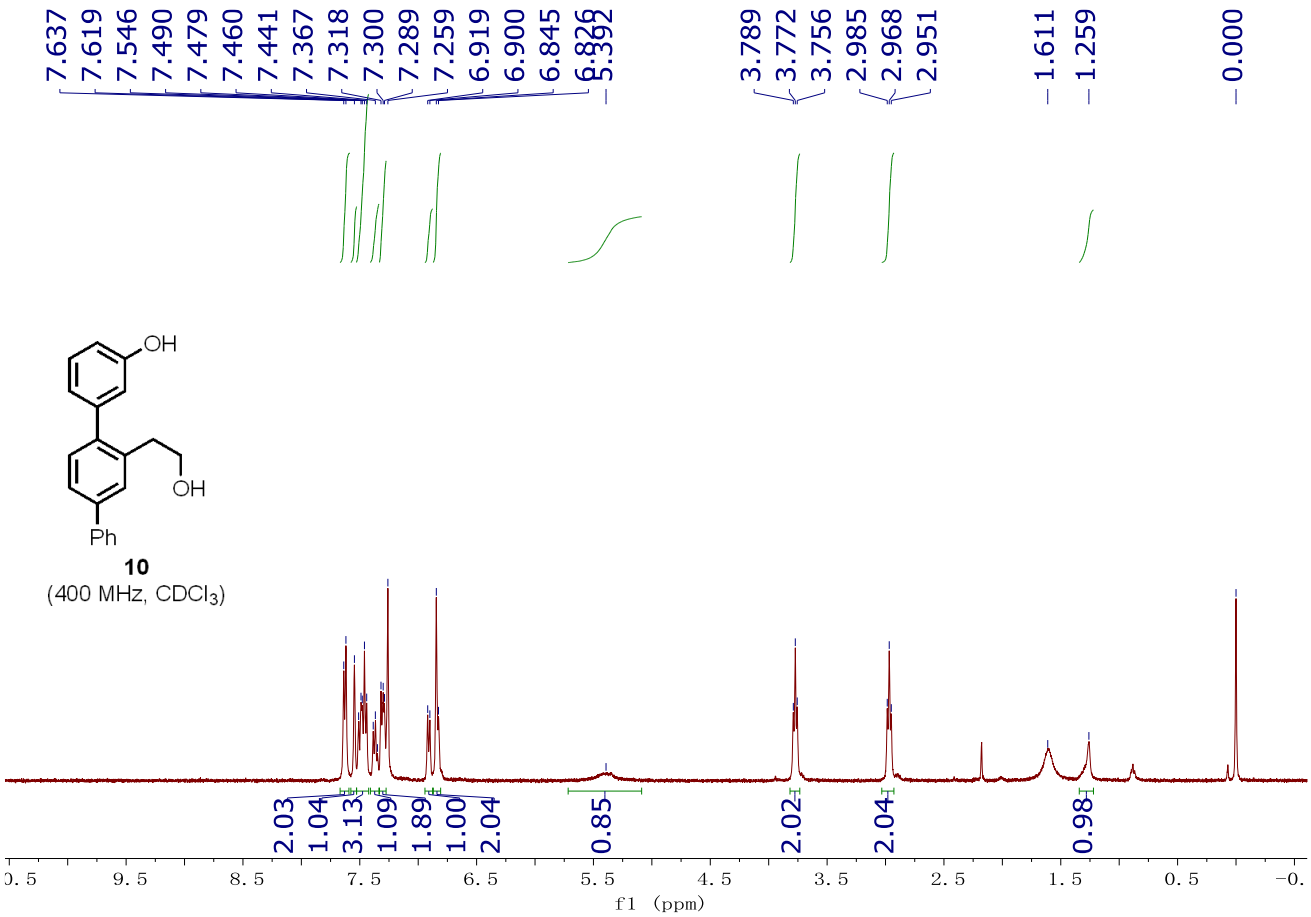

166.99
145.72
140.08
139.45
138.59
129.95
129.47
128.70
127.02
126.04
124.95
77.32
77.00
76.68
76.34
52.05
34.94
21.40
NH2
COOMe
6
(100 MHz, CDCl3)
f1 (ppm)

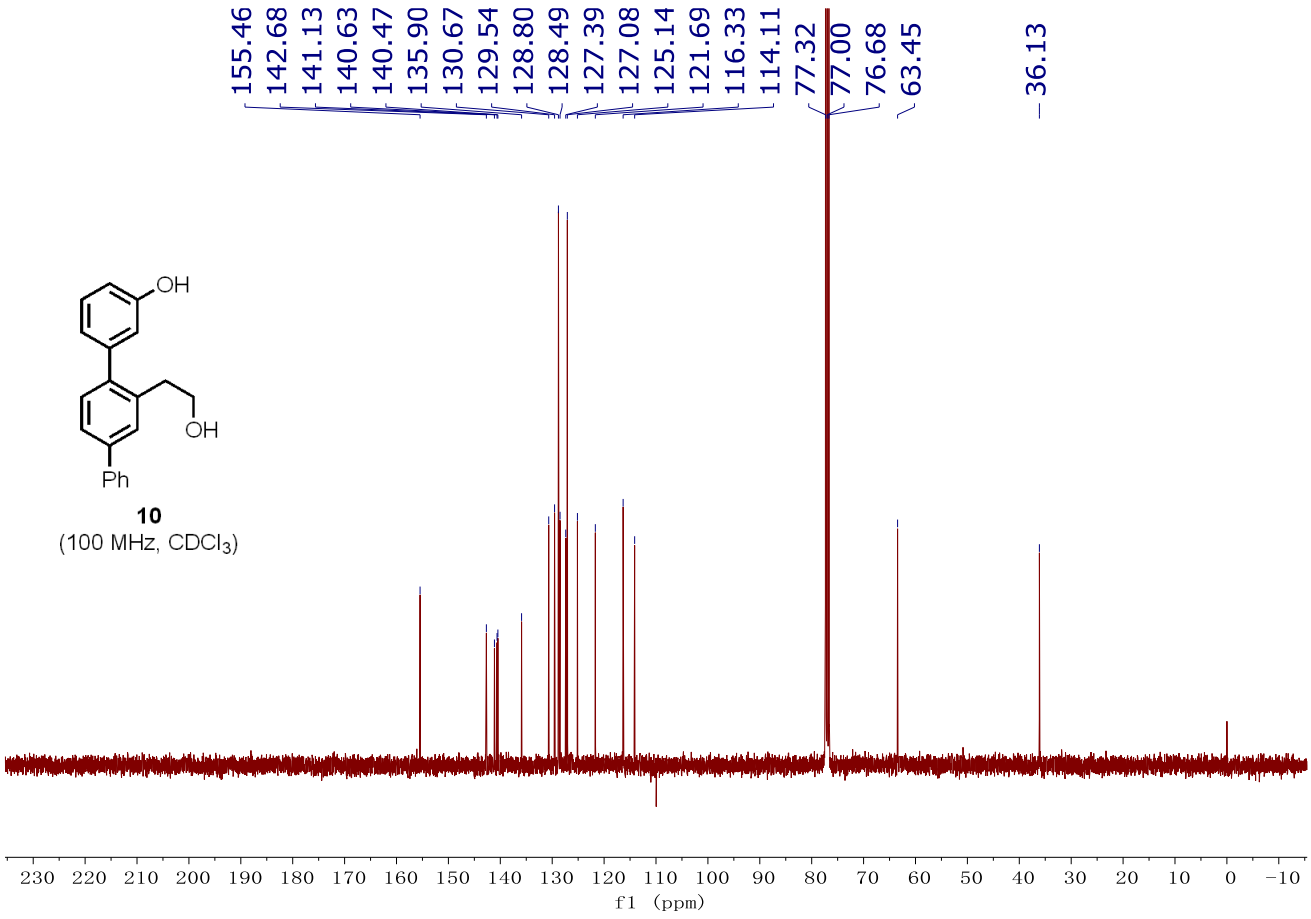

8.091
8.071
7.645
7.625
7.299
7.279
7.256
7.082
3.931
3.917
3.900
3.884
2.919
2.903
2.887
2.406
1.681
-0.000
OH
COOMe
7
(400 MHz, CDCl3)
2.00
2.05
0.94
1.01
1.00
2.82
2.09
2.05
3.05
1.25
f1 (ppm)

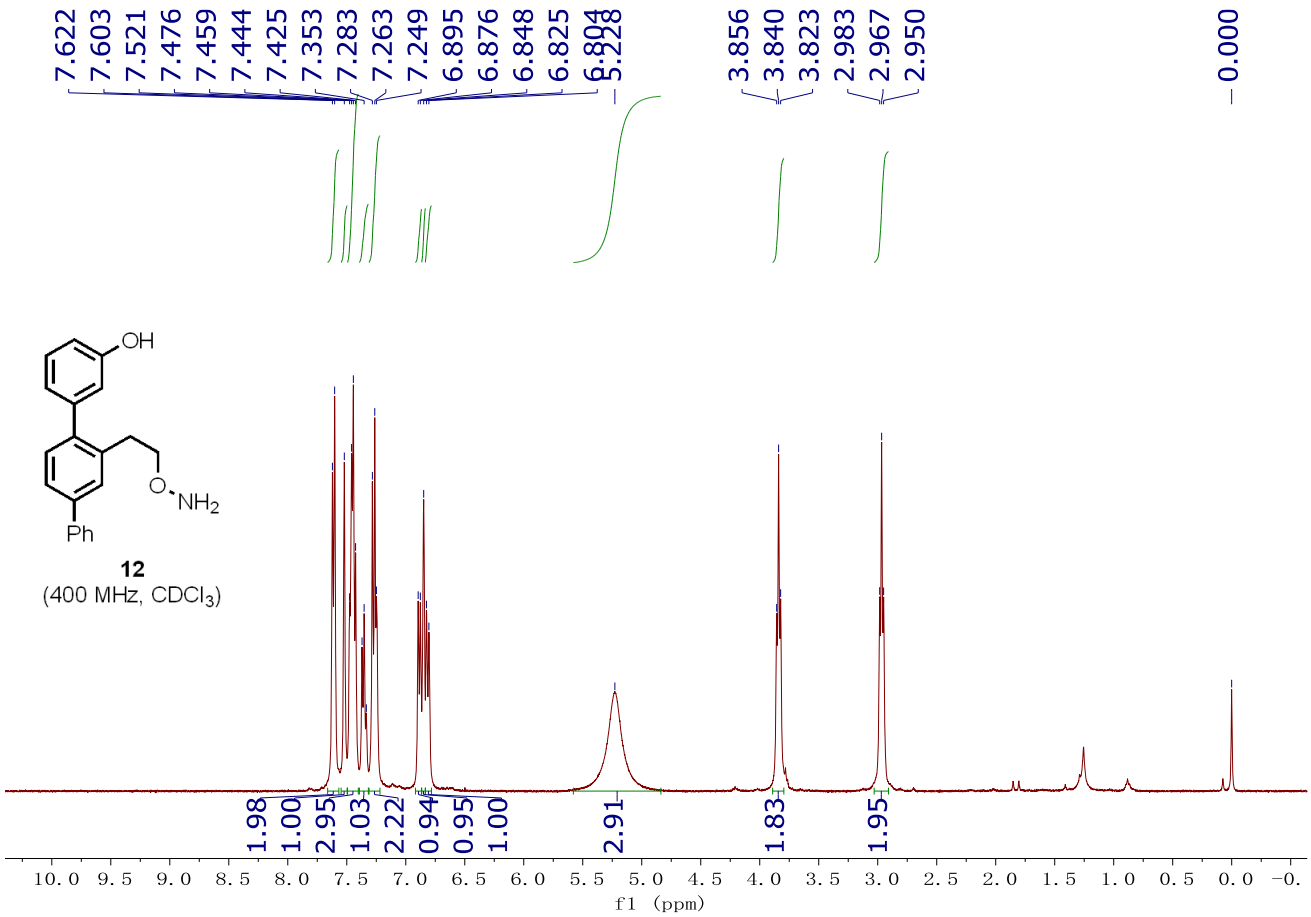

167.01
145.61
140.25
139.17
138.80
129.98
129.61
128.75
127.02
126.24
125.09
77.32
77.00
76.68
63.58
52.09
39.08
21.40
OH
COOMe
7
(100 MHz, CDCl3)
f1 (ppm)

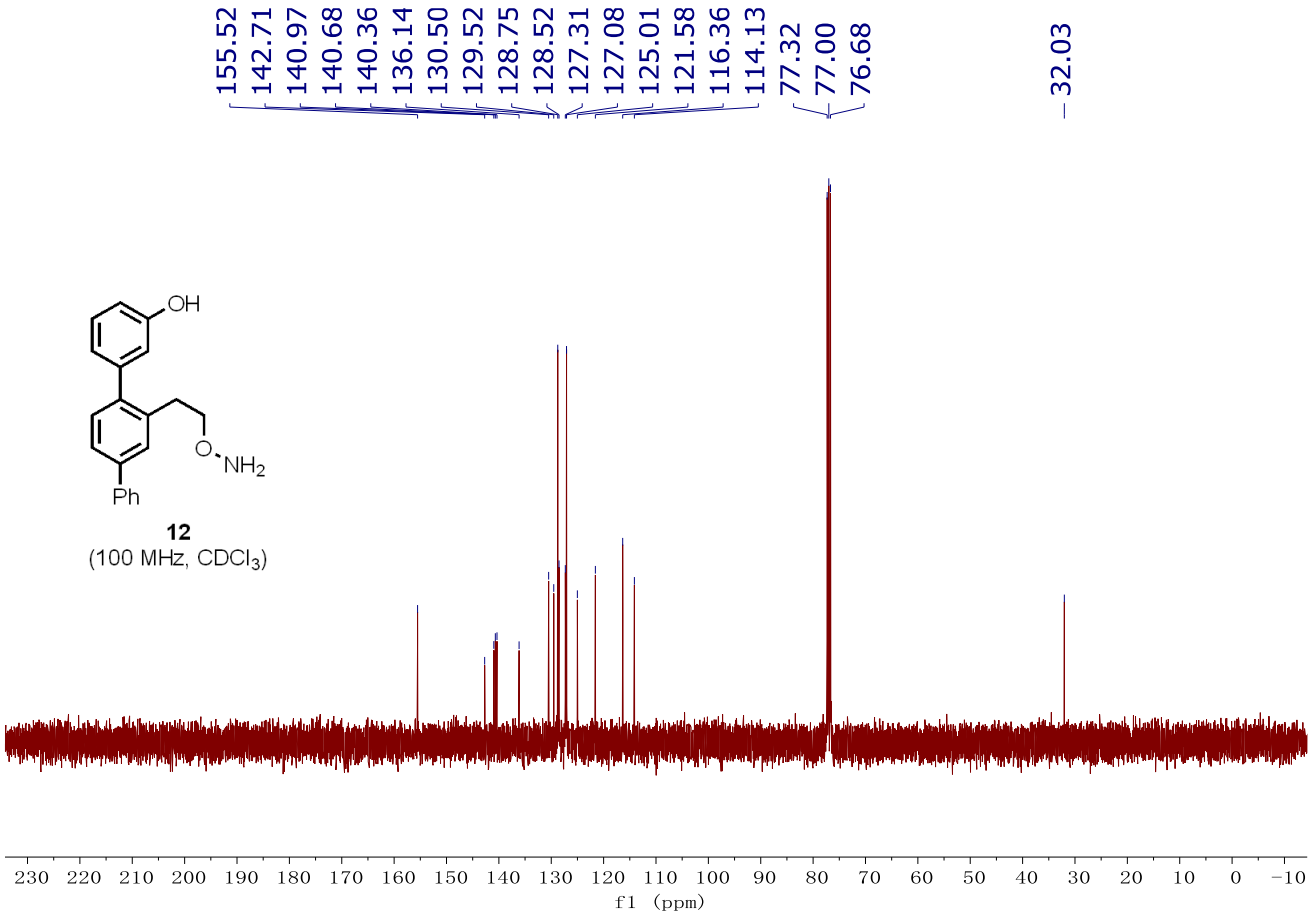

7.447
7.429
7.396
7.378
7.359
7.346
7.328
7.307
7.288
7.265
7.258
7.239
7.222
6.971
6.945
6.930
6.911
5.079
4.113
4.095
4.078
2.954
2.936
2.919
1.822
1.777
1.637
0.000
OBn
O
N
9
(400 MHz, CDCl3)
1.93
8.11
2.97
2.00
2.03
2.05
2.96
2.89
f1 (ppm)


158.44
154.57
143.08
142.08
136.94
136.20
129.91
129.90
129.07
128.53
127.90
127.46
127.29
125.98
122.05
115.74
113.42
77.32
77.00
76.68
73.57
69.95
32.59
21.82
15.66
OBn
O
N
9
(100 MHz, CDCl3)
f1 (ppm)


7.637
7.619
7.546
7.490
7.479
7.460
7.441
7.367
7.318
7.300
7.289
7.259
6.919
6.900
6.845
6.826
5.392
3.789
3.772
3.756
2.985
2.968
2.951
1.611
1.259
0.000
OH
OH
Ph
10
(400 MHz, CDCl3)
2.03
1.04
3.13
1.09
1.89
1.00
2.04
0.85
2.02
2.04
0.98
f1 (ppm)


155.46
142.68
141.13
140.63
140.47
135.90
130.67
129.54
128.80
128.49
127.39
127.08
125.14
121.69
116.33
114.11
77.32
77.00
76.68
63.45
36.13
OH
OH
Ph
10
(100 MHz, CDCl3)
f1 (ppm)


7.622
7.603
7.521
7.476
7.459
7.444
7.425
7.353
7.283
7.263
7.249
6.895
6.876
6.848
6.825
6.804
5.228
3.856
3.840
3.823
2.983
2.967
2.950
0.000
OH
O
NH2
Ph
12
(400 MHz, CDCl3)
1.98
1.00
2.95
1.03
2.22
0.94
0.95
1.00
2.91
1.83
1.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)


155.52
142.71
140.97
140.68
140.36
136.14
130.50
129.52
128.75
128.52
127.31
127.08
125.01
121.58
116.36
114.13
77.32
77.00
76.68
32.03
OH
O
NH2
Ph
12
(100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)